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POTENTIAL CHANGES IN CHLOROPLAST SUSPENSIONS AND IN WHOLE CYTOPLASM PREPARATIONS OF PLANT CELLS ON ILLUMINATION †*

By John D. Spikes, Rufus Lumry,‡ Henry Eyring and Robert Wayrynen

Division of Biology, Department of Chemistry, University of Utah, Salt Lake City

Communicated June 2, 1950

The investigation of the intermediate steps in the photosynthetic process has been difficult because of the inability to obtain photosynthesis in cell-free preparations. Any treatment which ruptures the plant cell membrane results in an almost complete loss of photosynthetic activity.[6] However, it appears that part of the photosynthetic reaction can be obtained with isolated chloroplasts or chloroplast fragments in the presence of added oxidants.[3] Upon illumination of such a system, water is oxidized with the production of oxygen gas and hydrogen ion while the added oxidant is reduced. No carbon dioxide is fixed in such preparations.[2] This reaction is now generally termed the Hill Reaction[6] and may be represented by the following equation when ferric iron is the added oxidant:

$$4Fe^{+++} + 2HOH \rightarrow 4Fe^{++} + O_2 \uparrow + 4H^+. \qquad (1)$$

Effective oxidants appear to include ferric oxalate,[3] *p*-benzoquinone,[10] various substituted quinones,[1] ferricyanide, chromate, and certain redox indicators.[5]

In past work the rate of the Hill reaction has been measured by observing oxygen evolution,[6] the reduction of methemoglobin,[3] hydrogen ion formation[4] and decolorization of redox indicators.[7] It appears from equation 1 that a change in the oxidation-reduction potential should occur as the reaction proceeds, which could be measured potentiometrically by the introduction of suitable electrodes into the chloroplast preparation. Since oxidation-reduction potentials can be determined rapidly and accurately this would appear to be a useful method for observing the reaction. In

the literature available to the authors, no reports of such a technique were found as applied to cell-free preparations, although potential changes upon illumination of living purple (photosynthetic) sulfur bacteria[8] and the algae Chlorella[9] have been observed.

Materials and Methods.—Whole cytoplasm preparations were made by blending green leaves in a small amount of isotonic sucrose in a Waring blendor. The blendate was filtered and briefly centrifuged to remove

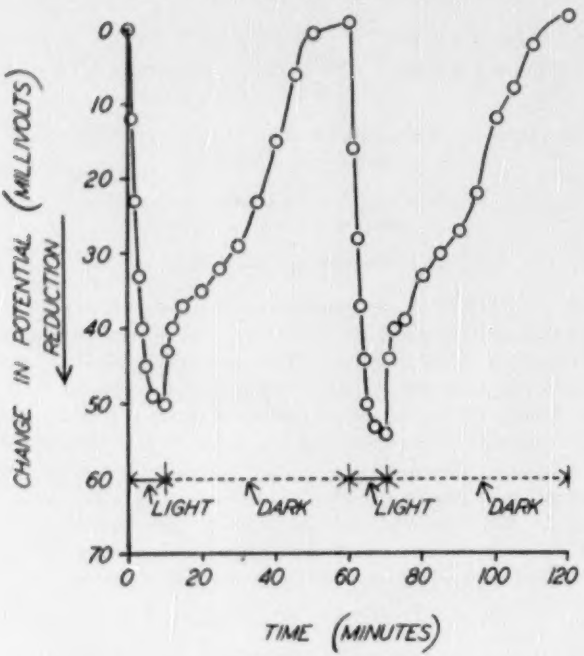

FIGURE 1

Curve showing potential changes in light and in dark of whole cytoplasm preparations of leaves of the wild sunflower (*Helianthus annuus*, L.) without added oxidant.

intact cells and large fragments of tissue. Chloroplasts were isolated by blending leaves as described above and then fractionating the blendate by differential centrifugation. The chloroplasts were resuspended in isotonic sucrose for use. For measurements the preparations were placed in small lucite cells provided with a back of platinum foil which served as one of the electrodes. A small hole connected the chamber of the cell to a side arm in which was inserted a small Beckman calomel electrode.

Experiments were routinely carried out at 4°C., and proper precautions were taken to prevent temperature changes in the cell during the illumination period. In most of the experiments the light was filtered through

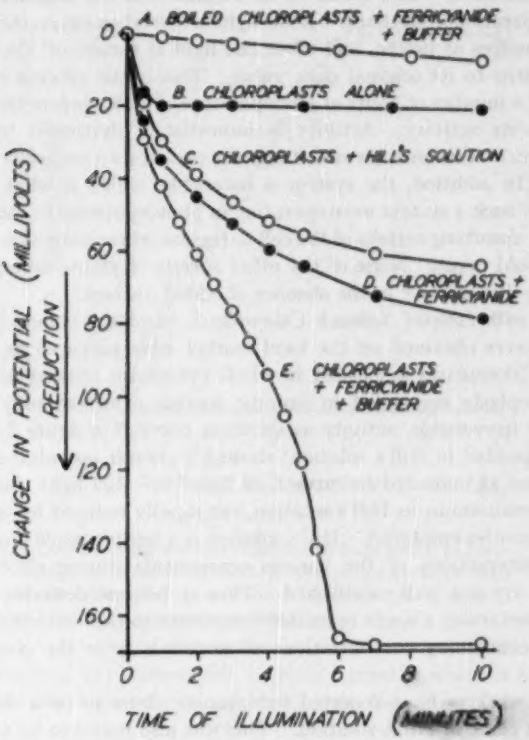

FIGURE 2

Curves showing the changes in potential upon illumination of suspensions of washed spinach chloroplasts under different conditions as indicated. Chloroplast concentration equal to 150 mg. of chlorophyll per liter. Potassium ferricyanide concentration 0.001 *M* where used. Potassium phosphate buffer concentration 0.1 *M*, pH 6.7, where used. Hill's solution as described in reference 4.

a Wratten A (red) filter which cut off all wave-lengths shorter than 5800 Å. Intensity of red light on the cell surface was approximately 5000 lux.

Whole Cytoplasm of Sunflower Leaves.—These preparations exhibited potential changes upon illumination as shown in figure 1. As the curve

indicates, there is a rapid change in potential upon illumination. The direction of the change shows that reduction is occurring. When the light is turned off, there is a more gradual change of the potential in the opposite direction, which levels off at a value near the original potential of the preparation in the dark. If the light is turned on again, the potential rapidly changes as before, and when the light is turned off the potential again returns to its original dark value. This cyclic process can be repeated for a number of hours at a temperature of 25°C. before the preparation loses its activity. Activity is immediately destroyed by boiling. This system is of interest because it appears to contain a naturally occurring oxidant. In addition, the system is reversible, which is what might be expected if such a system were operating in photosynthesis to carry energy from light absorbing regions of the cell to regions where reduction of carbon dioxide could occur. None of the other species of plants investigated to date show this activity in the absence of added oxidant.

Results with Isolated Spinach Chloroplasts.—Isolated chloroplasts from spinach leaves obtained on the local market were prepared as described above. Chloroplasts suspended in whole cytoplasm showed no activity, and chloroplasts suspended in isotonic sucrose exhibited only a slight, essentially irreversible, activity as shown in curve *B* of figure 2. Chloroplasts suspended in Hill's solution[4] showed a greater potential change on illumination as indicated in curve *C* of figure 2. Red light was used for these determinations as Hill's solution was rapidly reduced by white light of the intensities employed. Hill's solution is a fairly complicated mixture and the interactions of the various components during photochemical reduction are not well established. Thus it became desirable to use a medium containing a single reducible component so that calculations could be made concerning concentrations of materials from the observed potentials.

Several workers have reported ferricyanide alone to be a satisfactory oxidant in place of Hill's solution. This was also found to be true in the present work. Curve *D* in figure 2 shows the potential change upon illumination of spinach chloroplasts suspended in 0.001 *M* potassium ferricyanide. Red light was used in all experiments with ferricyanide as an oxidant, as ferricyanide alone showed a potential change when illuminated with white light. Curve *A*, figure 2, shows that boiling the chloroplasts destroyed all of the activity of this system.

A consideration of equation 1 shows that hydrogen ion is produced as the reaction proceeds. In unbuffered preparations this results in a rapid decrease in pH which inactivates the system. Curve *E* of figure 2 shows the potential change in a system containing spinach chloroplasts and 0.001 *M* ferricyanide buffered at pH 6.7 with 0.1 *M* phosphate buffer. The potential-time curve given by unbuffered systems is a typical logarith-

mic curve, while the buffered system gives a typical potentiometric titration curve plus a region where the potential rapidly assumes a constant value.

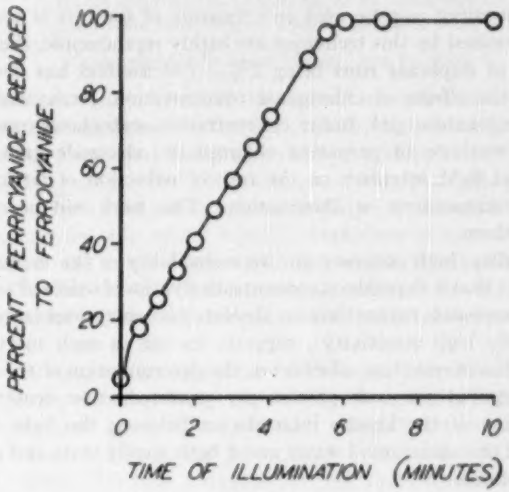

FIGURE 3

Curve showing per cent reduction of ferricyanide to ferrocyanide with time by washed spinach chloroplasts upon illumination. This curve is derived from the data of curve *E* of figure 2 by applying equation 4.

The amount of the ferricyanide originally present which is reduced to ferrocyanide with time may be calculated from the potential-time data as follows:

$$\text{ferrocyanide} \rightarrow \text{ferricyanide} + e \tag{2}$$

$$E = E^\circ - \frac{RT}{F} \ln \frac{(\text{ferricyanide})}{(\text{ferrocyanide})} \tag{3}$$

$$\%\ \text{ferricyanide reduced to ferrocyanide} = 100 \times \frac{1}{e^{-(F/RT)(E-E^\circ)} + 1} \tag{4}$$

where E is the observed potential, E° is the standard half-cell potential for the ferricyanide-ferrocyanide couple, F is the Faraday of electricity, R is the gas constant and T is the absolute temperature. Equation 4 may then be used to calculate the per cent reduction of ferricyanide correspond-

ing to each observed potential. The potential-time data of curve E of figure 2 are shown, as calculated on this basis, in figure 3. The conversion of ferricyanide to ferrocyanide is linear with time upon illumination up to a conversion of approximately 97% when the curve rapidly flattens. The slope of this curve may be used as a measure of the rate of the reaction. Rates determined by this technique are highly reproducible, the maximum variability of duplicate runs being 2%. The method has been used to determine the effects of chloroplast concentration, ferricyanide concentration, temperature, pH, buffer concentration, cytoplasm concentration, inhibitors, methods of preparing chloroplasts, electrode area, electrode position and light intensity on the rate of reduction of ferricyanide by chloroplast suspensions on illumination. This work will be reported in detail elsewhere.

The rapidity, high accuracy and reproducibility of the method coupled with the fact that it depends on concentration ratios of oxidized and reduced forms of compounds rather than on absolute concentrations (which permits an extremely high sensitivity), suggests its use in such matters as the determination of quantum efficiencies, the determination of the number of photons required per unit process per photoreduction center, and the determination of the kinetic interrelation between the light absorption process and the oxidation of water under both steady state and non-steady state conditions.

* This work was supported by the University of Utah Research Fund.

† This work was described in part in a paper presented at the Symposium on Reactions in Living Systems at the December, 1949 meetings of the AAAS.

‡ Merck Fellow in the Natural Sciences.

[1] Aronoff, S., *Plant Physiol.*, **21,** 393 (1946).

[2] Brown, A. H., and Franck, J., *Arch. Biochem.*, **16,** 55 (1948).

[3] Hill, R., and Scarisbrick, R., *Proc. Roy. Soc.* (*London*), **B129,** 238 (1940).

[4] Holt, A. S., and French, C. S., *Arch. Biochem.*, **9,** 25 (1946).

[5] Holt, A. S., and French, C. S., *Ibid.*, **19,** 368 (1948).

[6] Holt, A. S., and French, C. S., *Photosynthesis in Plants*, Ch. 14, Iowa State College Press, 1949.

[7] Macdowall, F. D. H., *Plant Physiol.*, **24,** 462 (1949).

[8] Roelofsen, P. A., *Proc. Kon. Akad.*, **37,** 660 (1934).

[9] Tang, P. S., and Lin, C. Y., *J. Cell. and Comp. Physiol.*, **9,** 149 (1936).

[10] Warburg, O., and Lüttgens, W., *Naturwiss.*, **32,** 161 (1944).

THE STRUCTURE OF THE $Mo_6Cl_{14}^{--}$ COMPLEX IN THE CRYSTAL $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$

BY PHILIP A. VAUGHAN

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Communicated by Linus Pauling, June 21, 1950

Cyrill Brosset has determined the crystal structures of the bipositive molybdenum compounds $(Mo_6Cl_8)(OH)_4 \cdot 14H_2O$[1] and $(Mo_6Cl_8)(Cl_4 \cdot 2H_2O) \cdot 6H_2O$[2] and has found that the basic structural unit for these compounds is a $(Mo_6Cl_8)X_6$ group in which X is oxygen or chlorine. The structure of this group can be visualized as follows (Fig. 1). The molybdenum atoms are at the corners of a nearly regular octahedron of edge 2.63 Å, eight chlorine atoms are at the corners of a symmetrically circumscribed cube such that the shortest Mo–Cl distance is 2.56 Å, and the six X atoms are at the corners of a larger octahedron, one X being bonded to each molybdenum atom.

Some years ago, at the suggestion of Professor Linus Pauling, I began an x-ray study of the compound $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$. It forms crystals with space group C_s^4-Cc and unit cell parameters $a_1 = 19.33$ Å, $a_2 = 14.93$ Å, $a_3 = 9.16$ Å, and $\beta = 115.2°$. The volume of the unit cell is 2390 Å.^{3} which, for four formulae per cell, leads to calculated density 3.12 g. cm.$^{-3}$, in good agreement with the observed density 3.09 g. cm.$^{-3}$, determined by flotation.

By applying the radial distribution method to a powder photograph of this compound, I have found that it contains the group $(Mo_6Cl_8)Cl_6^{--}$ with the structure described above. The intensity function used was

$$I'(s) = \sum_i I_i e^{-C(s-s_i)^2}, \qquad (1)$$

where I_i is visually estimated intensity of the ith powder line and $s = \frac{4\pi \sin \theta}{\lambda}$, θ being the Bragg angle. It is readily shown that, to a good approximation, $I'(s)$ is given by

$$I'(s) = K \sum_{i,j} A_{ij} \sin s r_{ij}, \qquad (2)$$

where

$$A_{ij} = \frac{\overline{f_i f_j}}{r_{ij}} e^{-(r_{ij}^2/4C)}.$$

The radial distribution integral was then calculated from the equation

$$rD(r) = \int_0^{s_{max}} e^{-0.5s^2} I'(s) \sin sr \, ds \qquad (3)$$

by means of the punched card technique developed in these Laboratories for electron diffraction investigations.[3] The radial distribution function is then interpreted in terms of the structure by the relationship

$$rD(r) = \sum_{i,j} \frac{A_{ij}}{4} \sqrt{\frac{\pi}{a}} e^{-[(r-r_{ij})^2/4a]}, \qquad (4)$$

the sum being over all of the non-zero distances in the proposed structure and A_{ij} being defined above. The function $I'(s)$ has the advantage that it is a smooth function of s and can therefore be treated in much the same

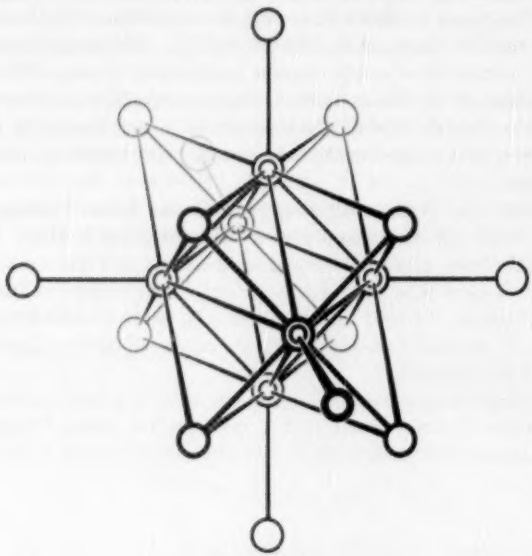

FIGURE 1

The $(Mo_6Cl_8)Cl_6^{--}$ ion, double circles are Mo atoms; single circles are chlorine atoms.

way as an electron diffraction scattering curve; for instance, theoretical $I'(s)$ curves can readily be calculated for any proposed structure by means of equation (2). The function $I'(s)$ and the radial distribution function obtained therefrom are shown in figure 2. The $(Mo_6Cl_8)Cl_6^{--}$ group would probably have, following the work of Brosset, the following parameters:

Shortest Mo–Mo	=	2.63 Å (average)
Mo–Cl (cubic Cl)	=	2.56 Å (average)
Mo–Cl (octahedral Cl)	=	2.43 Å

A radial distribution function corresponding to this model calculated from equation (4) is shown in figure 2. The agreement with the experimental radial distribution function is good, the only serious discrepancy out to about 5 Å being the greater height of the peak near 3.6 Å in the experimental curve. This is explained by the fact that there are additional

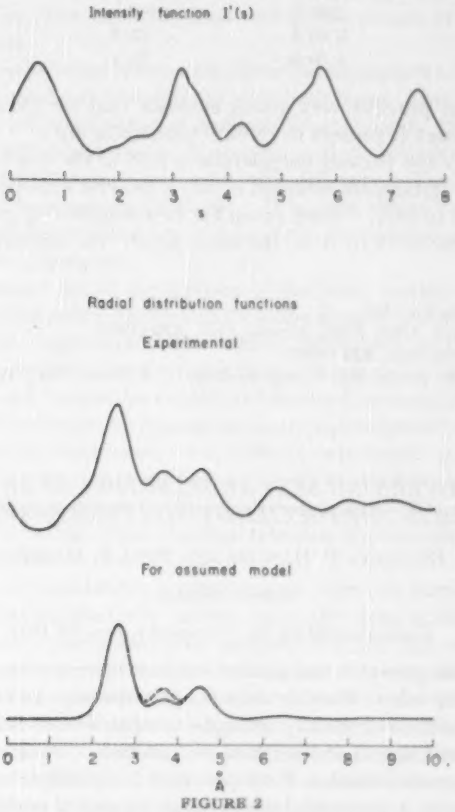

FIGURE 2

Intensity and radial distribution functions for $(NH_4)_2(Mo_6Cl_8)Cl_6 \cdot H_2O$.

Cl...Cl distances of about 3.60 Å in the crystal due to intermolecular contacts. If the reasonable assumption is made that each octahedral chlorine atom makes van der Waals' contact with six chlorines in different molecules and that each cubic chlorine atom makes contact with three,

the theoretical radial distribution function becomes as indicated by the dotted line in figure 2; the heights are now in excellent agreement. The positions and relative heights of the maxima less than 5 Å in the two radial distribution functions are

EXPERIMENTAL		THEORETICAL	
HEIGHT	POSITION	HEIGHT	POSITION
100	2.53 Å	100	2.59 Å
31.8	3.63 Å	32.0	3.65 Å
33.6	4.50 Å	34.4	4.50 Å

The agreement provides very strong evidence that the $(Mo_6Cl_8)X_4$ group found by Brosset is present in $(NH_4)_2(Mo_6Cl_8)Cl_4 \cdot H_2O$.

Space group and packing considerations lead to the conclusion that the $(Mo_6Cl_8)Cl_6^{--}$ groups are arranged in nearly directly superposed hexagonal layers parallel to (001). Each group has four neighboring groups at about 8.75 Å and two at 9.16 Å in the same layer; the interlayer spacing is 8.76 Å.

[*] Contribution No. 1432.

[1] Brosset, Cyrill, *Arkiv. Kemi, Mineral. Geol.*, **A20** (1945).

[2] Brosset, Cyrill, *Ibid.*, **A22** (1946).

[3] Shaffer, P. A., Schomaker, V., and Pauling, L., *J. Chem. Phys.*, **14**, 659–64 (1946).

FACTORS GOVERNING SEXUAL SELECTION AS AN ISOLATING MECHANISM IN THE POECILIID FISH LEBISTES RETICULATUS

BY CARYL P. HASKINS AND EDNA F. HASKINS

UNION COLLEGE

Communicated by Th. Dobzhansky, June 30, 1950

In a previous paper[1] it was pointed out that three species of small viviparous Poeciliid fishes, *Poecilia vivipara*, *Micropoecilia parae*, and *Lebistes reticulatus*, form an unusually intimate sympatric association in certain brackish coastal waters of the island of Trinidad. The geographic range of all three species is similar, *P. vivipara* and *L. reticulatus* being characteristic inhabitants of the coastal streams and lagoons of northeastern South America and the immediately adjacent islands, while *M. parae* is represented in the same mainland areas either by the typical species or by morphologically distinguishable but closely related forms. The ecological preferences of the three species are closely similar. All are primarily surface feeders in warm shallow waters. In Trinidad, *P. vivipara* and *M. parae* are confined to brackish coastal waters, while *L. reticulatus* is a common inhabitant of all bodies of water of any size, ranging from mountain streams

and inland ponds almost into the open sea. In the areas where their ranges coincide, the three species swim in mixed schools and feed in close association.

The females of all three species are generally similar in form, coloration, and habitus. All three species show pronounced sexual dimorphism, with brilliantly colored males which, unlike the females, differ markedly between species, both in form and coloration and in the details of courting and mating patterns.

Reproductive isolation between the three species appears to be essentially complete in nature. No intergrades have been found in any of the populations examined, amounting in total to approximately three thousand individuals. Hybrids between *P. vivipara* and *L. reticulatus* have been obtained in the laboratory, but only with difficulty. Though large and vigorous, they were apparently sterile. It is clear, therefore, that physiological isolating mechanisms are of importance in maintaining the species structure of the population.

The pronounced sexual dimorphism of the three species and the elaborate color and courtship patterns of the males suggest that sexual selection may also be of importance as an isolating mechanism in this sympatric association. Experiments reported in the paper referred to above indicated that the male of *L. reticulatus* may indeed exhibit a remarkably high degree of selectivity for conspecific females in mixed populations which have been in equilibrium for some time. No evidence was found in any of these observations, however, that the females of any of the three species exhibit a similar selective response to the appropriate males. Thus the predominant, if not the whole, share of sexual selection appears initially to reside with the male.

Two points of considerable interest emerge from this picture, neither of which could be satisfactorily settled from the data earlier presented. First, it seemed *a priori* somewhat unlikely that the high order of specificity in mate-selection which was found should rest with the male alone. It would seem more probable that the female exhibits complementary selective reactions, the whole behavior pattern of the two sexes then forming a chain of stimulation, such as has been reported by Tinberger and Van Iersel[2] for the stickleback. Certainly such complementary reactions in the female Lebistes are by no means evident, but it is entirely conceivable that they are of a kind not easily detected by the observer. The matter is of considerable importance in the interpretation of the evolutionary significance of the elaborate male patterns of color and behavior in these forms.

Second, it was observed in the earlier work that the choice-pattern of the male Lebistes was characteristically quite inefficient at the beginning of an experiment, and increased in accuracy rapidly as the experimental situation stabilized, reaching to as high as 95.5% of correct choices after one week.

This situation is susceptible of two quite different interpretations. On the one hand, it may be interpreted as the simple expression of an innate instinctive preferential reaction of male Lebistes to females of their own species which became progressively more clearly expressed as the males became adjusted to the environment of the experiments, this behavior replacing a higher, more generalized excitability in which random contacts tended to occur. Such an instinct pattern, of course, might be expected to be positively selected in evolution if interspecific sterility was general, or if the interspecific F1 hybrids showed lowered fertility over either parent in accord with the general principle of "conservation of gametes" originally stated by Dobzhansky and recently further elucidated by Mayr.[3] Both these conditions are fulfilled in populations of *P. vivipara*, *M. parae*, and *L. reticulatus*.

On the other hand, the improvement in efficiency of the male pattern of choice with time may result from a learning process, responsive to progressive conditioning of the male to "correct" as opposed to "incorrect" gonopodial contacts.

Both of these points are of considerable theoretical interest. Neither can be directly tested by experiments of the kind earlier described because of the factor of interspecific sterility. It seemed possible, however, that light might be shed on both questions through experiments of similar design in which the females of *M. parae* and *P. vivipara* were replaced by mutant females of Lebistes differing from the normal wild type only in single genes affecting body coloration. Races of Lebistes are available which exhibit such differences but are entirely interfertile, both among themselves and with the wild type, and in which the F1 progency exhibit fertility and viabilty differing little if any from that of the parents. The males of such races, moreover, exhibit courting and mating patterns identical with the wild type, and in permanently mixed cultures both sexes breed as readily with the wild type as within their own race. Work of this sort has proved feasible and suggestive.

The Experimental Material.—Nearly all the known genes for body coloration in Lebistes are both sex-linked and sex-limited, being expressed only in the adult male. A few, however, affecting the general body-color background rather than the male color patterns, are autosomal and are fully expressed in adults and young of both sexes. Two of these, named by Goodrich "Golden" and "Cream," were selected for this work.[4] Golden behaves as a single-factor autosomal Mendelian recessive to wild type, while Cream is allelic and recessive to it and to wild type. The mutation Golden in the homozygous condition produces a fish of bronze but not translucent ground-color, showing scattered patches of melanic pigment in the body and fins. Melanin is accumulated especially about the edges of the scales and in the underlying diamond pattern, resulting in a pro-

nounced accentuation of the normal reticulate markings of Lebistes. The mutation Cream when homozygous leads to an almost complete suppression of melanin in skin pigmentation. Frequently no pigmented melanophores are macroscopically visible, although a few are probably always present. As a result, Cream fish are without reticulation and of a translucent light yellow coloration. The males of both races exhibit typical sex-linked color patterns superposed on these backgrounds, in so far as the limited melanin available will permit. Both races are of normal form and behavior, differing from the species only in the rather marked alterations of background body color, which contrast conspicuously with the gray reticulate pattern of the wild type. Heterozygotes of both races with wild type are phenotypically indistinguishable from homozygous wild type. Heterozygotes of Golden and Cream are indistinguishable from Golden. Females of wild type, Golden, and Cream stocks carrying known sex-linked factors for male coloration (which of course were not phenotypically expressed) were used throughout the work.

Males of several stocks were used. Wild males or their progeny were drawn from stocks taken from the Maracas and Arima Rivers, the Nariva Swamp, and at Maracas Beach in Trinidad, and from water courses near Delaford in Tobago. The first two locations in Trinidad and the one in Tobago were freshwater streams where Lebistes normally occurs in the absence of the other species, while the latter two locations in Trinidad were brackish lagoons in which all three forms occur sympatrically.

In addition to these individuals from wild cultures taken directly from Trinidad and Tobago, males from other stocks were used. These included wild-type males from an aquarium race carrying the sex-linked gene Pauper, first obtained by Winge in 1922 from the West Indies, described by him in 1927[9] and kindly given to this laboratory in 1934. Wild-type males from three further stocks were also used. They were derived by twice backcrossing FI hybrids between a wild-type aquarium race carrying the male sex-linked gene Maculatus and wild Trinidad stock from the St. Joseph, the Marianito, and the Maracas rivers to the wild stock, thus producing a genetically marked culture of seven-eighths wild genic composition. The sex-linked gene Maculatus was originally described by Winge[10] and, like Pauper, was obtained by us from Winge in 1934. It has been carried in mass culture since that time.

Finally, several males of Golden and Cream races were used, particularly in conditioning experiments. They were taken from races in which these autosomal factors had been combined with the sex-linked genes Pauper and Maculatus described above, and with a third such factor, Armatus, obtained from Danish domestic stock by Winge in 1922, described by him in 1927, and likewise obtained through his generosity in 1934.

Experimental Procedure and Results.—The experimental method was

essentially an elaboration of that described earlier.[1] Several aquaria of varying capacity were arranged to simulate the natural environment. Tanks varied in capacity from ten to twenty gallons. Into such tanks three or six females were introduced simultaneously, one or two each of Wild-type, Golden, and Cream stocks. The females selected all contained developing embryos (the normal condition in the wild species) and were taken directly from mass cultures of their own races. Males, singly in some cases and in groups in other tests, were then introduced. With one class of exceptions, such males were taken directly from stock cultures of their own races. Wherever possible in each test, females of the races corresponding to the males used were taken from precisely the same cultures as these males. This factor did not prove critical, however. Counts were then made of the number of gonopodial contacts of the introduced males with the females of their own and of the other two races on the first and subsequent days.

The exceptional experimental procedure noted above was that obtaining in experiments with "conditioned" or "reconditioned" males (tables 3 and 4). Here young males were raised in isolation until sexual maturity was attained, after which they were exposed for a period of a month or longer to a female of another race than their own. Such males were then introduced directly from the "conditioning" to the experimental tank. A few experiments were also undertaken in an attempt to "recondition" males already "conditioned" to females of races other than their own. Such individuals were transferred from the experimental tank to a new "conditioning" one, containing a single female of a race other than that to which they had previously been conditioned, immediately after the initial observations. After a period of exposure of a month or more to the new environment, they were returned to the experimental tank for further observation.

The results are shown in the following tables.

TABLE 1

WILD-TYPE MALES

SERIES A

Males from Trinidad (Maracas and Arima Rivers, Nariva Swamp, Maracas Beach) and Tobago (Delaford). Also males from backcrosses of Maculatus and wild stock from the St. Joseph, Marianito, Maracas, and Arima Rivers in Trinidad

	TOTAL MALES	WILD-TYPE	GOLD	CREAM	TOTAL
Wild stock	20	630	75	20	725
Backcrossed stock	61	134	11	5	150
Total	81	764	86	25	875

SERIES B

Males from mass culture of Pauper, Wild-type

MALES	WILD-TYPE	GOLD	CREAM	TOTAL	
2	190	26	4	220	
83	954	112	29	1095	Experimental Totals
	365	365	365	1095	Expected Totals on Basis of Chance Contacts

TABLE 2

MALES OF MACULATUS CREAM, ARMATUS CREAM, PAUPER GOLD, AND ARMATUS GOLD, TAKEN FROM MASS CULTURE

TYPE	TOTAL MALES	WILD-TYPE	GOLD	CREAM	TOTAL
Maculatus Cream	17	73	35	221	329
Armatus Cream	5	44	11	70	125
Pauper Gold	5	64	19	17	100
Armatus Gold	5	44	53	44	141

	TOTAL MALES	"CORRECT"	"INCORRECT"	TOTAL
Experimental Totals	32	363	332	695
Expected Totals on Basis of Chance Contacts		231.7	463.3	695

TABLE 3

"CONDITIONED" MALES, AS SHOWN

MALE TYPE	WILD-TYPE	GOLD	CREAM	TOTAL
	"Conditioned" to Wild-type			
Armatus, Cream	92	2	6	100
Armatus, Cream	91	0	9	100
Maculatus, Cream	87	7	2	96
Armatus, Gold	95	5	0	100
	"Conditioned" to Gold			
Armatus, Cream	9	87	10	106
Maculatus, Cream	104	14	7	125*
Armatus, Gold	5	73	23	101
Armatus, Wild-type	9	74	22	105
	"Conditioned" to Cream			
Armatus, Wild-type	6	6	13	25
Maculatus, Wild-type	8	8	84	100

	TOTAL MALES	"CORRECT"	"INCORRECT"	TOTAL
Experimental Totals	10	710	248	958
Expected Totals on Basis of Chance Contacts		319.4	638.6	958

* This exception was further tested with a diminutive wild-type female. The results were confirmatory.

TABLE 4

"RECONDITIONED" MALES, AS SHOWN

TYPE OF MALE	INITIAL CONDITIONING	INITIAL REACTION		SECONDARY CONDITIONING	SECONDARY REACTION	
Armatus Cream	Female Gold, 11/11/49–12/25/49	Wild-type:	9	Female Wild-type, 1/1/50–2/22/50	Wild-type:	113
		Gold:	87		Gold:	5
		Cream:	10		Cream:	8
Armatus Cream	Female Wild-type, 10/14/49–12/26/49	Wild-type:	92	Female Gold, 12/31/49–2/19/50	Wild-type:	12
		Gold:	2		Gold:	0
		Cream:	6		Cream:	0
Armatus Cream	Female Gold,. 11/11/49–12/24/49	Wild-type:	5	Female Wild-type, 12/26/49–2/19/50	Wild-type:	5
		Gold:	73		Gold:	34
		Cream:	23		Cream:	23

These three males were all closely similar, from the same mass culture of small population, inbred for fifteen years. They were treated in closely similar fashions. Yet it will be noticed that the second and third did not alter their original conditioning, while the first, which had followed a schedule closely similar to the others, did so alter markedly—an indication of the probable psychological variability of the males in this respect.

It is probable that males of *L. reticulatus* in mass cultures of their own race typically make a high proportion of gonopodial contacts with the larger females present. This is in all probability an instinctive behavior pattern, which may well be a result of natural selection. Every effort was made, therefore, to "match" the sizes of females used in each series as closely as possible. Exact matching was not feasible, but the effect of variable female size, as against variable color, was further reduced by using each set of females in experiments with differently conditioned males, predominant male choice then shifting from one race of females to another in each set.

Females were measured and weighed at the end of each series in which they were used. Since wild-type females tend to grow somewhat more rapidly in mixed culture than the recessive mutants, they were usually a little larger at the end of the experiments, even if carefully matched at the beginning. In order to be certain that the tendency to an over-all predominance for contacts with wild-type females, later referred to, was not in fact a size effect, some parallel test experiments were run in which the wild-type female used was conspicuously the smallest. The results were the same: males which showed a predominant tendency to contact the slightly larger wild-type female showed a similar predominance of contact with the markedly smaller one.

The weights and the lengths, measured from the snout to the base of the caudal peduncle, of the various series of females used are shown below.

Discussion.—In all, observations were made on the behavior of 125 wild-type Lebistes males from wild cultures taken from four representative localities in Trinidad, from aquarium-bred stocks and from backcross hybrids of these, and from aquarium stocks of several cultures of two races

differing from the wild type only in single autosomal recessives for body-coloration. A total of 2748 gonopodial contacts was recorded. Several interesting points emerged, which suggest possibly significant answers to the questions earlier raised.

It will be noticed from table 1 that wild-type males taken from mass culture exhibited remarkably good discrimination in differentiating between females of their own constitution and those of the two recessive races. This was true whether the males were actually wild individuals, individuals derived from wild cultures, of long inbred aquarium stocks, or were backcross hybrids between wild and laboratory stocks. Furthermore, this pronounced selectivity was exhibited toward any wild-type female, whether or not it was derived from the same specific stock as the wild-type male. Thus it was evidently the body color of the female which served as the basis of male discrimination.

TABLE 5

MEASUREMENTS OF FEMALES USED IN COMPETITIVE TESTS

FEMALE GROUP		WEIGHT, G.	LENGTH (SNOUT TO BASE OF CAUDAL FIN), MM.
I.	Wild-type	...	28.0; 23.0 (Six females were used
	Gold	...	25.0; 25.0 in this group)
	Cream	...	25.0; 24.0
II.	Wild-type	0.75	32.0
	Gold	0.47	28.0
	Cream	0.65	28.5
III.	Wild-type	0.38	27.8
	Gold	0.32	27.1
	Cream	0.34	27.0
IV.	Wild-type	0.21	23.5
	Gold	0.07	22.9
	Cream	0.10	22.9
V.	Wild-type	0.75	32.0
	Gold	0.47	28.0
	Cream	0.65	28.5

The data recorded in table 2 indicate that males of Golden and Cream stocks taken from mass cultures of their own races exhibit a considerably better order of discrimination for females of those races than would be expected. It is of great interest, however, that their choice-pattern does not approach the perfection of that shown for wild-type females by wild-type males. This point was emphasized when observations were made on "conditioned" males, as shown in table 3. Of the ten conditioned males used, nine showed a choice of higher than expected accuracy for the females to which they had been conditioned, irrespective of their own genetic constitution. This appears to indicate rather definitely that the choice-pattern is at least in part a "learned" reaction, conditioned by the initial

exposure of the young male, and that in the absence of further conditioning factors it may be quite tenaciously retained.

In the presence of further conditioning factors, choice behavior may be modified much later in the life of the male, though the evidence of this is still incomplete. This is shown in table 4. The three males recorded there were of closely similar constitution. All were taken as immature fish from a small mass culture long inbred, and were given identical treatment throughout. It is of interest, therefore, that the first showed a pronounced modification of its original behavior, while the second and third adhered throughout to their initial patterns of conditioning.

A further point of interest emerges from these data. It will be noticed from table 3 that, although nine of the ten "conditioned" males showed an accuracy of choice higher than expectancy for the females to which they had been conditioned, this accuracy was not so good for males conditioned *away* from wild-type as in those conditioned *toward* wild-type. This is shown more effectively in table 6 in which all the data have been classified on the basis of conditioning toward or away from the wild-type.

TABLE 6

RELATIVE CHOICE EFFICIENCY OF MALES "CONDITIONED" TO WILD-TYPE AND TO OTHER BODY COLORS

"CONDITIONING"	"CORRECT"	"INCORRECT"	TOTAL	
Wild-type	1319	172	1491	Experiment
Wild-type	497	994	1491	Theoretical
Other	708	549	1257	Experiment
Other	419	838	1257	Theoretical

Total Contacts Recorded: 2748
Total Males Observed: 125

It will be seen that the differences are marked. It is clear from this data, and more evident in the data of table 4, that this difference cannot be attributed to a superior sensory endowment of the wild-type over the mutant male, for mutant males conditioned to wild-type responded as efficiently in their choice of wild-type females as did wild-type males conditioned to mutant females in their choice of the latter. It seems more probable that in addition to the conditioned, "learned" reaction, disposing the conditioned male to a predominance of contacts with females of the race to which it has been habituated, there is also another component, disposing the male, whatever its conditioning, to predominate in contacts with wild-type females. It is not clear at present what this component is.

Lastly, it seems evident from these experiments that complementary choice-patterns in the female, if they exist at all, cannot be of determining importance nor can a reaction-chain between male and female such as that

described for the stickleback have great significance in Lebistes. For it would not be expected that notable deviations of behavior-pattern would distinguish the females of the three color races of Lebistes used, nor could any such deviations in fact be observed. It seems extremely probable, therefore, that mate selection was made entirely by the male and that this discrimination was effected on the basis of vision, the body color or total body reflectivity of the female being of prime importance.

Although differences such as total body reflectivity are thus evidently determining for males confronted with choices between wild-type and mutant females of their own species, under other circumstances male discrimination may be accomplished with a high order of accuracy as a response to distinctions apparently much less conspicuous. This was early suggested by the ultimate high specificity of male discrimination between wild-type Lebistes females and the very similarly colored females of *M. parae* reported in the paper earlier cited.[1] In view of the present results, it became of interest to test it further. A choice situation was therefore set up for wild-type Lebistes males conditioned to wild-type Lebistes females between a female of *M. parae* on the one hand, and a mutant Lebistes female, which, as shown, would ordinarily be rejected in favor of a wild-type Lebistes female, on the other.

Sixteen wild-type Lebistes males taken from a mass culture of wild-type Maculatus stock twice backcrossed to wild Trinidad stock from the Arima River were given the choice between a typical female of *M. parae* and a Maculatus Cream female of Lebistes. The results on three days are shown in table 7. It will be seen that they agree closely with the choice patterns earlier reported between *M. parae* and wild-type Lebistes females. A rapid period of learning was exhibited, and within one week the choice, which originally favored *M. parae*, became 98% perfect for the Lebistes

TABLE 7

RELATIVE CHOICE EFFICIENCY OF WILD-TYPE LEBISTES MALES "CONDITIONED" TO WILD-TYPE FEMALES BETWEEN FEMALES OF *M. parae* AND MUTANT LEBISTES

Sixteen males of wild-type *Maculatus* stock, twice backcrossed to wild stock from the Arima River, Trinidad, taken from wild-type mass culture. Exposed to one wild female of *M. parae* and one female of Maculatus Cream, domestic stock, taken from mass culture of Maculatus Cream

ELAPSED TIME FROM INTRODUCTION	CONTACTS WITH *M. parae*	CONTACTS WITH MACULATUS CREAM
Day of introduction (n)	49	26
$n + 1$	2	23
$n + 7$	2	08

Length (snout to base of caudal fin) of *M. parae* female: 25.0 mm.
Length (snout to base of caudal fin) of *Lebistes* female: 24.0 mm.

Weight of *M. parae* female: 0.35 g.
Weight of *Lebistes* female: 0.31 g.

female, even though it was a mutant which would normally have been rejected, and was somewhat smaller and lighter in weight than the female of *M. parae*. Clearly neither size nor the rather close approximation of females of *M. parae* to the color pattern of wild-type female Lebistes (which appears to the human eye much closer than to the mutant Lebistes female) are as determining in choices of this sort as is conspecificity of the female. It is quite possible that minute behavioral factors in the female may be involved here. The predominance of contacts with the *M. parae* female during the first hours, however, strongly suggested in this case, as in the experiments earlier reported, that conditioning on the part of the male was most important, very probably involved with the mechanism of gonopodial contact.

Thus it would appear that in nature sexual discrimination of Lebistes for females of their own species, as contrasted with those of two superficially very similar species, is excellent, and that it is a contributing factor in maintaining specific isolation in the intimately sympatric associations of these species which occur in the brackish lagoons of Trinidad. It would appear that such discrimination is effected predominantly by the male, the female being essentially a passive agent. It is effected predominantly by visual means. This situation may throw suggestive light on the evolutionary significance of the brilliant and variable sex-associated color patterns so characteristic of Lebistes males, which should possibly be interpreted as primarily of intrasexual warning rather than of intersexual display value in natural selection.

The discrimination is in part a learned and "plastic" reaction, achieved through initial conditioning and subject to modification by later opposed conditioning, at least in certain individuals. In part, however, it appears to be innate and instinctive, and to have been established through natural selection. In nature, of course, these two components must reinforce one another to secure a predominance of contacts of male Lebistes with females of that species in the intimate sympatric associations in which it may exist.

Summary and Conclusions.—Earlier studies have indicated that males of *L. reticulatus* exhibit excellent powers of discrimination for females of their own species against those of two very similar related forms, *P. vivipara* and *M. parae*, which exist sympatrically with Lebistes in certain Trinidad waters. Such discrimination may constitute an important isolating mechanism for the species. The fact that the three species are largely intersterile in laboratory crosses and apparently hybridize very rarely in nature, however, makes a detailed examination of the mechanism of this discrimination difficult.

Experiments are described in which the accuracy of discrimination of Lebistes males between females of three races of the same species differing

in a single autosomal factor for body coloration is tested. This procedure is adapted to shed further light on certain aspects of the process. Observations were made in total on 141 males, involving counts of 2948 gonopodial contacts. The following conclusions seem justified:

1. Measuring the reaction of the male Lebistes to females of its own and other color races by the relative frequency of gonopodial contacts, a rather good discrimination by males for females of their own race can be demonstrated.

2. This discrimination obtains in males of all three autosomal color races of Lebistes used.

3. The discrimination is made predominantly or entirely by the male. There is no evidence of the existence of a chain of reactions between male and female, such as has been demonstrated for the stickleback.

4. The discrimination is predominantly or entirely visual.

5. In part, the discrimination is a "learned" reaction, which can be specifically modified by conditioning. The reaction of a male of any given race is decisively affected by its previous experience. Such discrimination is not a function of the genetic constitution of the individual male. Males which have been conditioned as young fish to one set of reactions can sometimes be later retrained to another, but the response to such retraining is variable.

6. Although males conditioned to wild-type females show marked preponderance of choice for wild-type females over the color mutants used, such mutants are preferred to wild females of *M. parae*, after an initial "learning" period. Thus the behavior pattern of such males follows closely that earlier reported in discrimination between wild females of Poecilia and Micropoecilia and of wild or wild-type Lebistes.

7. In part, the discrimination appears to be an innate, instinctive reaction, predisposing the male, whatever its own experience or genetic constitution, to make predominant contact with wild-type Lebistes females. Experiments of the type described could probably determine the relative importance of the learned and the instinctive components in the observed performance. In nature, the two components will be mutually reinforcing to produce a very efficient isolating mechanism for the species.

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[1] Haskins, C. P., and Haskins, E. F., "The Role of Sexual Selection as an Isolating Mechanism in Three Species of Poeciliid Fishes," *Evolution*, **3**, 160–169 (1949).

[2] Tinbergen, N., and Van Iersel, J. J. A., "Displacement Reactions in the Three-Spined Stickleback," *Ibid.*, **1** (1), 56 (1947).

[3] Mayr, Ernst, "The Bearing of the New Systematics on Genetical Problems. The Nature of Species," *Advances in Genetics*, **2**, 217 (1948).

[4] These body-color alleles to wild-type were described by Goodrich, *et al.*,[5] Winge and Ditlevsen,[6] Haskins and Druzba,[7] and Haskins and Haskins.[8]

[5] Goodrich, H. B., Josephson, N. D., Trinkaus, J. P., and Slate, Heanne M., "The Cellular Expression and Genetics of Two New Genes in *Lebistes reticulatus*", *Genetics*, **29**, 584–592 (1944).

[6] Winge, Ø., and Ditlevsen, E., "Colour Inheritance and Sex Determination in *Lebistes*," *Heredity*, **1**, 65 (1947).

[7] Haskins, C. P., and Druzba, J. P., "Note on Anomalous Inheritance of Sex-Linked Color Factors in the Guppyi," *Am. Nat.*, **72**, 571–574 (1938).

[8] Haskins, C. P., and Haskins, E. F., "Albinism, a Semi-lethal Autosomal Mutation in *Lebistes reticulatus*," *Heredity*, **2**, 251–262 (1948).

[9] Winge, Ø., "The Location of Eighteen Genes in *Lebistes reticulatus*," *J. Genetics*, **18**, 1–43 (1927).

[10] Winge, Ø., "One-Sided Masculine and Sex-Linked Inheritance in *Lebistes reticulatus*," *Ibid.*, **12**, 145–162 (1922).

ON THE MULTIPLICATION OF S-FUNCTIONS

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The functions which furnish the characters of the irreducible representations of the full linear group have been named, in honor of I. Schur, S-functions. If m is any non-negative integer and if n is the dimension of the linear group there is associated with each partition of m into not more than n parts: $m = \lambda_1 + \lambda_2 + \ldots + \lambda_k$, $k \leqslant n$, $\lambda_1 \geqslant \lambda_2 \geqslant \ldots \geqslant \lambda_k$, an irreducible representation, of degree m, of the full linear group whose characters were determined by Frobenius. Let $z_1, \ldots, z_n$ be the characteristic numbers of any element of the n-dimensional linear group; then the character $[\lambda_1, \lambda_2, \ldots, \lambda_k]$, of the representation in question, which corresponds to this element is the quotient of two n-rowed determinants whose elements are powers of the characteristic numbers $z_1, \ldots, z_n$. The element in the pth row and qth column of the determinant in the numerator is z_q raised to the power $\lambda_p + n - p$ (it being understood that, if $k < n$, $\lambda_p = 0$ if $p > k$) and the element in the pth row and qth column of the determinant in the denominator is z_q raised to the power $n - p$ (so that the determinant in the denominator is the familiar Vandermonde determinant of the n numbers $z_1, \ldots, z_n$). If, now, we have two representations of degrees m_1 and m_2, respectively, of the full linear group, the product of their characters, i.e., of the corresponding S-functions, furnishes the character of a representation of degree $m_1 + m_2$, in general reducible, of the full linear group (which representation is known as the Kronecker

product of the two given representations of the full linear group). It is with the problem of analyzing this product into its irreducible components that we concern ourselves in the present note. A rule furnishing this analysis was stated by Littlewood and Richardson in 1934[1] and proved by Robinson in 1938.[2] This rule involves the construction of appropriate diagrams of partitions of $m_1 + m_2$ from the diagrams of the given partitions of m_1 and m_2, respectively. A different method, based on a recurrence process, was given by us in 1937.[3] We point out now that a slight and obvious modification of Frobenius' formula for the characters of the irreducible representations of the full linear group furnishes, in what seems to us the simplest way, from the theoretical point of view, the desired analysis of the Kronecker product of any two of these irreducible representations. In the preparation of a table of products of Schur-functions, however, the recurrence process has definite advantages, particularly when m_1 and m_2 are large.

If we multiply the numerator of Frobenius' formula by Vandermonde's determinant (using row multiplication) we obtain an n-rowed determinant whose elements are sums of powers of the n characteristic numbers $z_1, \ldots, z_n$. On denoting by $s(p)$ the sum of the pth powers of these n numbers: $s(p) = z_1^p + z_2^p + \ldots + z_n^p$, $p = 0, 1, 2, \ldots$, the element in the pth row and qth column of the resulting product is $s(\lambda_p + 2n - p - q)$. The product of the denominator of Frobenius' formula by Vandermonde's determinant (i.e., the square of Vandermonde's determinant) is the n-rowed determinant of which the element in the pth row and qth column is $s(2n - p - q)$. On reversing the order of the columns in both numerator and denominator we have the following result:

The characters $\{\lambda_1, \ldots, \lambda_n\}$ of the irreducible representation, of degree m, of the full linear group which are associated with the partition $\lambda_1 \geqslant \lambda_2 \geqslant \ldots \geqslant \lambda_n \geqslant 0$ of m are the quotients of two n-rowed determinants; the element in the pth row and qth column of the determinant in the numerator is $s(\lambda_p + n - p + q - 1)$ while the element in the pth row and qth column of the determinant in the denominator is $s(n - p + q - 1)$.

The same argument shows that the characters of the Kronecker product of the two irreducible representations of the full linear group which are associated with the partitions $\lambda_1 + \ldots + \lambda_k = m_1$, $k \leqslant n$, $\mu_1 + \mu_2 + \ldots + \mu_j = m_2$, $j \leqslant n$, of m_1 and m_2, respectively, is the quotient of two n-rowed determinants whose elements are power sums of the n characteristic numbers $z_1, \ldots, z_n$. Of these the element in the pth row and qth column of the determinant in the denominator is again $s(n - p + q - 1)$ while the element in the pth row and qth column of the determinant in the numerator is $s(\lambda_p + \mu_{n-q+1} + n - p + q - 1)$. Thus all we have to do, in order to analyze the Kronecker product of the two given irreducible representations of the full linear group, is to analyze the determinant of which the element

in the pth row and qth column is $s(\lambda_p + \mu_{n-q+1} + n - p + q - 1)$ into a sum of determinants in each of which the element in the pth row and qth column is of the type $s(\lambda_p' + n - p + q - 1)$ where $\lambda_1' \geqslant \lambda_2' \geqslant \ldots \geqslant \lambda_n'$ is a partition, involving not more than n elements, of $m_1 + m_2$. To do this we consider the product $s(\lambda_1 + n - 1)s(\lambda_2 + n - 2)\ldots s(\lambda_n)$ and introduce n operators $x_1, \ldots, x_n$ which are such that x_q, $q = 1, 2, \ldots, n$, increases by 1 the argument of the qth of the n factors of this product. Thus the result of operating on $s(\lambda_1 + n - 1)\ s(\lambda_2 + n - 2)\ldots s(\lambda_n)$ by $x_1^{p_1}x_2^{p_2}\ldots x_n^{p_n}$ is $s(\lambda_1 + p_1 + n - 1)\ldots s(\lambda_n + p_n)$. Then the determinant of which the element in the pth row and qth column is $s(\lambda_p + \mu_{n-q+1} + n - p + q - 1)$ is the result of operating on $s(\lambda_1 + n - 1)\ldots s(\lambda_n)$ by the determinant of which the element in the pth row and qth column is x_p raised to the power $\mu_{n-q+1} + q - 1$. This determinant is the product of the Vandermonde determinant of the operators $x_1, \ldots, x_n$ by the Schur function of these operators which is associated with the partition $\mu_1 \geqslant \mu_2 \geqslant \ldots \geqslant \mu_j$ of m_2. The result of operating on $s(\lambda_1 + n - 1)\ldots s(\lambda_n)$ by the Vandermonde determinant of the operators $x_1, \ldots, x_n$ is the n-rowed determinant of which the element in the pth row and qth column is $s(\lambda_p + n - p + q - 1)$. All we have to do, then, to obtain the desired analysis of the Kronecker product of the two given irreducible representations of the full linear group is to write out $\{\mu_1, \ldots, \mu_j\}$ as a symmetric function (of degree m_2) of the operators $x_1, \ldots, x_n$ and to operate with this symmetric function on $\{\lambda_1, \ldots, \lambda_n\}$. The expression of $\{\mu_1, \ldots, \mu_j\}$ as a symmetric function of the operators $x_1, \ldots, x_n$ is readily carried out by the method explained on page 164 of my book *Theory of Group Representations*.[4] In carrying out the calculations it is well to take $n = m_1 + m_2$; this furnishes the analysis for all values of $n \geqslant m_1 + m_2$. If $n < m_1 + m_2$ we must discard all partitions of $m_1 + m_2$ which contain more than n non-zero elements. All disordered partitions must be rearranged in the usual way.

Example.—Analyze the square of the Schur-function $\{2, 1\}$. Here $m_1 = m_2 = 3$ and we take $n = 6$. Thus we write $\{2, 1\}$ in the form $\{2, 1, 0, 0, 0, 0\}$. From the table on page 154 of my book[4] we read off

$$\{2, 1\} = \sum_{i,j} x_i^2 x_j + 2\sum_{i,j,k} x_i x_j x_k.$$

Hence

$$\{2, 1\}\{2, 1\} = \{4, 2\} + \{4, 1^2\} + \{3^2\} + \{2^3\} - \{3, 1^3\} - \{2^2, 1^2\} - 2\{2, 1^4\} + 2\{3, 2, 1\} + 2\{3, 1^3\} + 2\{2^2, 1^2\} + 2\{2, 1^4\} = \{4, 2\} + \{4, 1^2\} + \{3^2\} + 2\{3, 2, 1\} + \{3, 1^3\} + \{2^3\} + \{2^2, 1^2\}.$$

This result is valid if $n \geqslant 4$; if $n = 3$ we must reject $\{3, 1^3\}$ and $\{2^2, 1^2\}$; if $n = 2$ we have $\{2, 1\}\{2, 1\} = \{4, 2\} + \{3^2\}$. The case $n = 1$ cannot arise since $\{2, 1\}$ has more than one non-zero element.

[1] Littlewood, D. E., and Richardson, A. R., *Phil. Trans. Roy. Soc.*, **A233**, 99–141 (1934).

[2] Robinson, G. de B., *Amer. Jr. Math.*, **60**, 745–760 (1938).

[3] Murnaghan, F. D., *Ibid.*, **59**, 437–488 (1937).

[4] Murnaghan, F. D., *Theory of Group Representations*, The Johns Hopkins Press (1938).

THE NON-FINITIZABILITY OF IMPREDICATIVE PRINCIPLES

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An impredicative class is a class definable only by reference to a totality to which the class itself belongs. Usual systems of set theory contain principles which provide us with infinitely many ways of generating such classes. We shall prove that we cannot in general replace these by finitely many, as we can in the case of predicative classes. In order to render the proof and what we prove clearer, we shall concentrate our attention on a rather special simple case. It will be obvious that other cases can be treated similarly.

Let L be the system determined by Bernays's axioms[1] I–III and Va. This is a system with finitely many axioms. Roughly speaking, in L we are assured that all finite classes obtained from the empty class by applying (any finite number of times) the operations of forming unit classes and sum classes are sets (membership-eligible classes), that every subclass of a set is a set, and that we have all predicative classes of these sets. Bernays has shown in detail that, by identifying natural numbers with certain sets of L, we can obtain the usual number theory in L.

For our purpose, we may describe L in the following manner. L contains the first-order predicate calculus (quantification theory) for one kind of variables X, Y, etc. (whose range consists of all classes) and an additional two-place predicate ϵ (membership). Since sets are merely classes which can be members of classes, variables ranging over sets can be introduced by contextual definitions such as: $(x)\phi x$ stands for $(X)((\exists Y)(X \epsilon Y) \supset \phi X)$. It follows immediately that if $(X)\phi X$ then $(x)\phi x$. Let us agree further that $X = Y$ stands for $(x)(x \epsilon X \equiv x \epsilon Y)$

The axioms of L can be stated thus:[2]

A1. $x = y \cdot x \epsilon Z \cdot \supset y \epsilon Z$.

A2. $(\exists x)(y)(y \epsilon x \equiv y \neq y)$.

A3. $(\exists x)(y)(y \epsilon x \equiv \cdot\ y \epsilon z \vee y = w)$.

A4. $(\exists x)(y)(y \epsilon x \equiv \cdot\ y \epsilon z \cdot y \epsilon X)$.

A5. $(\exists B)(x)(x \in B \equiv (\exists y)(\exists z)(x = \langle y\, z\rangle \cdot y \in z))$.
A6. $(\exists B)(x)(x \in B \equiv (\exists y)(\exists z)(x = \langle y\, z\rangle \cdot z \in A))$.
A7. $(\exists B)(x)(x \in B \equiv (\exists y)(\langle y\, x\rangle \in A))$.
A8. $(\exists B)(x)(x \in B \equiv (\exists y)(\exists z)(\exists w)(x = \langle y\, z\, w\rangle \cdot \langle z\, w\, y\rangle \in A))$.
A9. $(\exists B)(x)(x \in B \equiv (\exists y)(\exists z)(\exists w)(x = \langle y\, z\, w\rangle \cdot \langle z\, y\, w\rangle \in A))$.
A10. $(\exists B)(x)(x \in B \equiv \cdot\, x \doteq A \cdot x \doteq C)$.

It is known that within L we can derive from A5–A10 the following general principle which covers them as special cases:

P1. If ϕ is normal, then $(\exists B)(x)(x \in B \equiv \phi(x, X_1, \ldots, X_k))$. In other words, the system determined by A1–A4 and the predicative principle P1 can be finitized.

Let us now consider the system Q determined by A1–A4 and, instead of P1, the following impredicative principle:[3]

P2. If ϕ is any propositional function, then

$$(\exists B)(x)(x \in B \equiv \phi(x, X_1, \ldots, X_k)).$$

We want to prove that if Q is consistent, we cannot derive P2 (with the help of A1–A4) from any finite number of its special cases.

The proof depends essentially on the fact[4] that the classes declared to exist by any (finite or infinite) number of special cases of P2 can be enumerated by treating these axioms as operations for generating new classes from given ones. It turns out that when we take only a finite number of special cases of P2, the enumeration of the classes declared to exist can be expressed in Q. So that we can define by the diagonal method a new class which is provided by P2 but does not occur in the enumeration. Consequently, no finite number of operations determined by special cases of P2 could generate all the cases of P2.

In order to exhibit the line of reasoning more clearly, we shall give within Q an enumeration[5] of the classes required by the axioms of L. Then it will be obvious that other systems can be treated in a similar fashion.

The following are six fundamental operations answering to the axioms A5–A10.

1.1. $F_0(X, Y) = E$.
$F_1(X, Y) = V \times X$.
$F_2(X, Y) = D(X)$.
$F_3(X, Y) = Cnv_2(X)$.
$F_4(X, Y) = Cnv_3(X)$.
$F_5(X, Y) = -(X + Y)$.

Since we can develop number theory in Q, we can introduce variables m, n, etc., whose range consists of all natural numbers, and obtain ordinary

arithmetic functions. Consider now all the ordered triples $<m\ q\ k>$ $(m < 6)$ of natural numbers and define in Q the following ordering relation S for them:

1.2. $<m\ q\ k>\ S\ <i\ j\ p>$ for $m, i < 6$: $q = j \cdot k = p \cdot m < i \cdot \vee \max\{q, k\} < \max\{j, p\} \vee \cdot \max\{q, k\} = \max\{j, p\} \cdot k < p \cdot \vee \cdot \max\{q, k\} = \max\{j, p\} \cdot k = p \cdot q < j$.

With the help of S we can correlate the ordered triples $<m\ q\ k>$ $(m < 6$ with natural numbers by defining in Q (applying the usual technique o converting recursive definitions) a function J such that:

1.3. $J(0) = <0\ 0\ 0>$;
$J(n') =$ (the ordered triple $<m\ q\ k>$ such that $(m < 6 . (i)(j)(p)$ $(J(n)\ S <i\ j\ p> \equiv \cdot <m\ q\ k> = <i\ j\ p> \vee <m\ q\ k>\ S <i\ j\ p>))$

Next we define in Q three functions $K_i{}'n$ $(i = 1, 2, 3)$ which give the ith members of the triple $J(n)$:

1.4. $K_1{}'n = m$ for $(\exists k)(\exists j)(J(n) = <m\ k\ j>)$.
$K_2{}'n = k$ for $(\exists m)(\exists j)(J(n) = <m\ k\ j>)$.
$K_3{}'n = j$ for $(\exists m)(\exists k)(J(n) = <m\ k\ j>)$.

Using these auxiliary notions, we can define in Q by induction a function F such that:[6]

1.5. $K_1{}'n = 0 \supset \vec{F}'n = \vec{F}_0(F'K_2{}'n, \vec{F}'K_3{}'n)$;

. . . . . .

$K_1{}'n = 5 \supset \vec{F}'n = \vec{F}_5(F'K_2{}'n, \vec{F}'K_3{}'n)$.

The formal definition in Q for this function F can be stated thus:

1.6. $G(m, B)$ for $D(B) = \{0, \ldots, m\} \cdot (k)(k \leq m \supset : K_1{}'k = 0 . \vec{B}'k = F_0(\vec{B}'K_2{}'k, \vec{B}'K_3{}'k) \cdot \vee \cdot K_1{}'k = 1 \cdot \vec{B}'k = F_1(\vec{B}'K_2{}'k, \vec{B}'K_3{}'k) \cdot \vee \cdot \ldots \cdot \vee \cdot K_1{}'k = 5 \cdot \vec{B}'k = F_5(\vec{B}'K_2{}'k, \vec{B}'K_3{}'k))$.

1.7. $<x\ n> \in F$ or $x \in \vec{F}'n$ for $(\exists B)(G(n, B) \cdot <x\ n> \in B)$.

It should be easy to see that by applying induction on n we can prove in Q the six cases of 1.5 for the function defined in 1.7.

Then the enumeration of the classes which are declared to exist by the axioms of L is provided by the propositional function R:

1.8. $R(X, j)$ for $\vec{F}j = X$.

Hence, the classes declared to exist by the axioms of L are merely the classes X of Q such that $(\exists j)R(X, j)$.

Let us refer to a propositional function of Q as the translation of one of L if the former is obtained from the latter by restricting the class variables to range over classes X for which $(\exists j)R(X, j)$, or, in other words, by substituting $(X)((\exists j)R(X, j) \supset \phi X)$ for $(X)\phi X$. Then, by applying 1.5, we can prove in Q the translations A1′–A10′ of the axioms A1–A10 of L. Moreover, it is also easy to see that the translation of any theorem of L is a theorem of Q. Hence, if the translation of a certain particular theorem of Q (which is of course also a propositional function of L) is not provable in Q, then the given theorem of Q is not a theorem of L.

Now we prove that if Q is consistent, then the following theorem of Q is not provable in L:

$$(\exists B)(n)(n \in B \equiv n \in \vec{F}n). \tag{1}$$

Thus, let M be the class defined by (1). If (1) were provable in L, then its translation would be provable in Q and we would be able to prove in Q: $(\exists j)R(M, j)$. However, by using the usual argument for Cantor's theorem, we can prove in Q: $\sim(\exists j)R(M, j)$. Thus, if $R(M, i)$, then, by 1.8 and (1), $(k)(k \in \vec{F}i \equiv k \in \vec{F}k)$. Therefore, we would have: $i \in \vec{F}i \equiv i \in \vec{F}i$, a contradiction. Hence, we have:[3]

THEOREM I. *If Q is consistent, then the theorem (1) of Q is not provable in L.*

It follows that the following theorem of Q is also not provable in L:

$$(\exists C)(x)(n)(<x\ n> \in C \equiv (\exists B)(G(n, B)\cdot <x\ n> \in B)). \tag{2}$$

This is so because, if (2) were provable in L, (1) would also be. However, for each given number m, we can prove in L a theorem:

$$(\exists C_m)(x)(n)(<x\ n> \in C_m \equiv (\exists B)(G(m, B)\cdot (y)(j)(j > m \supset <y\ j> \in B)\cdot <x\ n> \in B)). \tag{3}$$

This may be seen as follows. Obviously we can prove (3) when m is 0. If we can prove (3) for the case when m is $n - 1$, then we can use C_{n-1} and prove (3) for the case when m is n.

But in the sequence consisting of C_0, C_1, etc., each class contains all its predecessors, and the class defined by (2) is just the union (sum class) of them. Therefore, we get:

THEOREM II. *If Q is consistent, then there exists a monotone increasing sequence of classes such that each of these classes can be shown to exist in L but that their union cannot.*

Similarly, if L' is any system which contains as axioms, besides A1–A4, merely finitely many (say j) special cases of P2, then we can define relations

and functions and prove theorems which are similar to those given in 1.1–1.8, with j replacing 6. It will be a routine matter to construct and prove these definitions and theorems for any given system L'. The only definition which calls for some comment is the one answering to 1.6, which, unlike 1.6 itself, may contain bound class variables when expanded. However, since in Q we allow all propositional functions in defining classes, such a change will not affect[8] the proving of theorems that answer to I and II. We have:

THEOREM III. *If Q is consistent, then the theorem of Q which is related to L' as (1) is to L is not provable in L'.*

THEOREM IV. *If Q is consistent, then there exists a monotone increasing sequence of classes such that each of these classes can be shown to exist in L' but that their union cannot.*

Theorem IV seems to indicate a special kind of incompleteness for all systems which contain merely a finite number of special axioms of class formation.

From III, we obtain:

THEOREM V. *If Q is consistent, then P2 cannot be reduced (with the help of A1–A4) to any finite number of its special cases.*

We can prove a similar theorem for each system which contains P2 and, instead of A1–A4, certain other axioms serving similar purposes. Let us refer to[9] a system of Quine and two systems of the present author as the systems K, M and N. We have:

THEOREM VI. *If K (or M or N) is consistent, then P2 cannot be reduced to any finite number of its special cases.*

Before concluding, we note that by similar arguments, we can also prove the non-finitizability of the impredicative principles in systems containing classes of classes, etc. For example, let us take the system P used by Gödel.[10] If $T_n (n > 1)$ is the part of P which includes the variables and classes up to the type n but nothing higher, then we have:

THEOREM VII. *If T_n is consistent, then its principles of class formation (Komprehensionsaxiome) cannot be reduced to any finite number of their special cases.*

It follows immediately:

THEOREM VIII. *If the simple theory of types P is consistent, then its principles of class formation are not reducible to any finite number of their special cases.*

Similarly, in spite of the fact that we can obtain an extension of the Zermelo set theory with finitely many axioms by distinguishing between sets and classes, we can prove the following theorem:

THEOREM IX. *If Zermelo's set theory (with its axiom of infinity) is consistent, then the Aussonderungsaxiom in it cannot be reduced to any finite number of its special cases.*

We want to thank Professor Quine for valuable criticisms and suggestions.

[1] Bernays, P., *J. Symbolic Logic*, **2**, 65–77 (1937); **6**, 1–17 (1941); **7**, 133–145 (1942).

[2] Unless otherwise explained, the notations and terminology will follow Gödel, K., *The Consistency of the Continuum Hypothesis*, Princeton, 1940. In particular, a normal propositional function will be a formula in which all bound variables are set variables or a formula equivalent to one such.

[3] This principle P2 has first been introduced by Quine, W. V. See his *Mathematical Logic*, Cambridge (Massachusetts), 1947 (2nd printing). P2 is his principle *202 on p. 162.

[4] This seems to have been first pointed out by Skolem, Th. (*Skrifter Norske Videnskaps-Akad. Oslo. I. Mat. Naturv. Klasse*, **1929**, No. 4). Later R. Carnap also stressed this fact (*The Logical Syntax of Language*, London and New York, 1937, especially p. 207 ff). However, Carnap seems to overlook the circumstance that among the axioms he considers the Aussonderungsaxiom, unlike the others, actually embodies an infinite number of constructional operations.

As Skolem has pointed out (*Ibid.*), such an enumeration in general does not provide us with a consistency proof of the system under consideration, because we do not know whether we can divide all the pairs $<M\ N>$ (M, N being any two classes from the given enumerable totality) into two domains of ϵ-pairs and non-ϵ-pairs (according as M belongs to N or not) in such a way that all the theorems of the system will be satisfied. However, in the case of the system L where only certain sets (for which we can easily exhibit a model) and predicative classes of them are required by the axioms, the enumeration can actually be made in a natural fashion to provide an enumerable model (and therewith a consistency proof) for the system. An immediate consequence of this point has been used by J. Barkley Rosser and the present author (see their joint paper to appear soon in *J. Symbolic Logic*), and, independently, by A. Mostowski (in a talk referred to at bottom of p. 70, *J. Symbolic Logic*, **15** (1950)).

[5] This follows closely the construction in Gödel's monograph, op. cit., p. 35. However, our task is easier, because we have a fixed universe of sets all through our process of generating new classes.

[6] The class $\hat{F}y$ is the class of all sets x such that $<x\ y> \epsilon F$. In order to avoid appeal to classes of classes, we are in 1.5–1.7 labeling the members instead of the classes themselves. A similar device has been employed under different circumstances by both Bernays (op. cit., p. 137) and Professor W. V. Quine (in his lectures, Spring, 1948).

[7] We observe incidentally that since L is known to have an enumerable model anyway, we could have used more direct arguments and proved in place of I a stronger theorem I′: (1) is not provable in L. However, our present proof has the advantage of being applicable to other cases to be considered below.

[8] If L' contained infinitely many special cases of P2 as axioms, then we would not be able to obtain a definition answering to 1.6 because we would need an infinite disjunction (whatever that may mean) or variables ranging over classes of classes which transcend the system Q. This is also the reason why we cannot adapt the arguments for proving Theorem I to derive a contradiction from the axioms of Q.

[9] See, respectively, Quine's book, op. cit., p. 154; *J. Symbolic Logic*, **13**, 129–137 (1948); *Ibid.*, **15**, 25–32 (1950).

[10] It is a system of type theory with natural numbers as individuals. See Gödel, K., *Monatsh. Math. Phys., Vienna*, **38**, 173–198 (1931).

ELECTROMAGNETIC PONDEROMOTIVE FORCES WITHIN MATERIAL BODIES

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Synopsis.—In classical electromagnetism the electrical force acting on a charged probe or small body is operationally defined as that force which must be added to the assumedly completely observable mechanical forces to restore otherwise failing classical particle mechanics. For a large body, rigid or non-rigid, lying in empty space, we may also define a total electromagnetic ponderomotive force as that force which added to the presumably observable total mechanical force restores otherwise failing mechanics. For such a body the total electromagnetic force thus operationally defined, may be determined by applying Maxwell's stress tensor in the empty space surrounding the body.

Very generally it is believed that specifically electromagnetic ponderomotive forces, volume and surface, exist within material bodies. Presumably these electromagnetic forces are to be defined by balancing properly with the mechanical stress tensor within the body.

One may attempt to define this mechanical stress tensor through the mechanical force required to keep the strain unchanged on making a cut along an element of surface within the body. However, in an electromagnetic field the force so obtained is not derivable from a tensor.

We may define as a possible electromagnetic stress tensor any tensor whose components are functions of the field vectors, **E**, **D**, **H** and **B**, and the charge and current densities ρ and **i**, and which in empty space, i.e., where $\mathbf{E} = \mathbf{D}$, $\mathbf{H} = \mathbf{B}$, $\rho = 0$, and $\mathbf{i} = 0$ reduces to Maxwell's electromagnetic stress tensor. Then we define the associated mechanical stress tensor through the vector difference between the calculated electrical surface force for the sides of the cut, and the mechanical force observed there, this difference being derivable from a tensor.

These two largely arbitrary tensors meet all the requirements of mechanics and electromagnetism and no experiment can distinguish between the validities of the various sets of such possible tensors. There is then no physically significant uniquely definable volume and surface electromagnetic ponderomotive force within a material body.

For the interior of a material body in an electric field, a net force tensor may be defined which gives the observable net volume forces, and net forces on surfaces of discontinuity. This net force tensor may be calculated from the volume energy density when such volume energy density exists.

I. Definition of Total Electromagnetic Ponderomotive Force for Particles and Isolated Bodies.—Classical electromagnetism, the electromagnetism of macroscopic bodies, begins with the theory of electrical ponderomotive forces acting upon particles. It is found by experiment that under certain conditions the classical mechanics of these small macroscopic bodies fails. This classical mechanics asserts that for such a small body we must have

$$m\mathbf{a} = \mathbf{F}_m \tag{1}$$

where m is the mass, $\mathbf{a}$ the acceleration, relative to a suitable frame of reference and $\mathbf{F}_m$ the resultant "mechanical" force acting on the particle. $\mathbf{F}_m$ is asserted to be completely determinable from observations on the state of contiguous macroscopic bodies, as for example the twist of the suspension string, and the strain in the supporting bar of a Coulomb experiment, and from the gravitational action of remoter bodies. When electrical phenomena appear, equation (1) fails, and we *define* $\mathbf{F}_e$, the electromagnetic ponderomotive force on the particle, as that vector which restores (1) giving

$$m\mathbf{a} = \mathbf{F}_m + \mathbf{F}_e. \tag{2}$$

Experience then shows that $\mathbf{F}_e$ thus defined can, in a wide variety of cases, be expressed at any point in space empty except for the particle and the means for impressing the mechanical force, $\mathbf{F}_m$, by the equation

$$\mathbf{F}_e = q\left(\mathbf{E} + \frac{1}{c}[\mathbf{v} \times \mathbf{H}]\right) \tag{3}$$

where the scalar q depends on the previous preparation of the particle, and $\mathbf{E}$ and $\mathbf{H}$ are vectors in space independent of q and $\mathbf{v}$, the velocity of the particle. q, $\mathbf{E}$ and $\mathbf{H}$ are thus *defined* by equation (3) except for a multiplicative constant which may then be fixed by some arbitrarily chosen operational definition of the unit of q.

Thus these definitions of $\mathbf{F}_e$, q, $\mathbf{E}$ and $\mathbf{H}$ through the failure of mechanics, rest on the assumption that the mechanical forces which act on the particle are completely known, and that the means for exerting these mechanical forces may have no influence on the electromagnetic field, that is that $\mathbf{F}_e$, q, $\mathbf{E}$ and $\mathbf{H}$ will be independent of the particular means for effecting $\mathbf{F}_m$.

The wide variety of cases referred to above can be described generally as occurring when the dimensions of the small body or particle are small enough compared to the distances from other bodies, excluding the means for impressing the force $\mathbf{F}_m$, and when the small body is prepared so as to make q small enough.

For a large macroscopic body, rigid or non-rigid, mechanics also makes a general assertion, namely that

$$\frac{d}{dt}\mathbf{M} = \mathbf{F}_m \tag{4}$$

where $\mathbf{M}$ is the total momentum of the body, and $\mathbf{F}_m$ is the total impressed mechanical force, which is determinable from the observations of the strains in contacting bodies, and the gravitational action of remoter bodies.

Again in the electromagnetic field (4) fails. Again, we may define a total electromagnetic ponderomotive force, $\mathbf{F}_e$, as that which restores (4) so that

$$\frac{d}{dt}\mathbf{M} = \mathbf{F}_m + \mathbf{F}_e \tag{5}$$

and again, for this definition to have meaning with content, we must assume that means are available for impressing $\mathbf{F}_m$ which do not affect the electromagnetic field, i.e., which give the same $\mathbf{F}_e$ independent of the means used for effecting the $\mathbf{F}_m$.

II. Limitation of This Paper to Steady Electric Fields.—While the author believes that the conclusions given in this paper are completely general, for the sake of brevity he will limit their exposition to the case of steady electric fields, and therefore to the case of bodies at rest, without electric currents.

III. Maxwell's Stress Tensor and Isolated Bodies.—Given a body, at rest, lying in empty space and in an electric field. The body is subjected to mechanical forces of the type referred to in Section I, which do not influence the field, and which give a total mechanical force $\mathbf{F}_m$ which may not be zero. $\mathbf{F}_e$ for this case, is then defined as $-\mathbf{F}_m$.

Surround the body by a closed surface S. $\mathbf{E}$ defined in Section I, is known at all points of S. Then, according to Maxwell (1), we have

$$\int_S \int \frac{1}{8\pi}\left(2\mathbf{E}\mathbf{E}\cdot d\mathbf{S} - \mathbf{E}^2\, d\mathbf{S}\right) = \mathbf{F}_e. \tag{6}$$

We shall not take the space here to establish Maxwell's equation (6). A way of doing so would be to postulate certain additional properties of charged small bodies or macroscopic particles as given by experiment, and to show then that (6) holds if the only matter within the surface S is a finite number, though possibly very large, of such charged particles at rest. We then postulate that the Maxwell field theory is a successful "local action" theory, and that therefore (6) must hold irrespective of the actual nature of the material system within S.

We may not pass from the case of the system of charged particles to that of a continuous body by asserting that such a body may be regarded

as being in any meaningful sense a very dense system of charged macroscopic particles. If we proceed to cut a macroscopic larger body into smaller and smaller macroscopic parts, we do not get particles in the sense used in previous paragraphs, because the dimensions of these individual smaller parts do not become small compared to the distance to the neighboring smaller parts. It is only when we reach the microscopic world of electrons and nuclei that this aspect of particles is reached. But at this point macroscopic mechanics loses its meaning, and with it also classical electromagnetism. Certainly, according to our present ideas of the quantum mechanics which governs the microscopic particles, electrons and nuclei, there is no "mechanical force" acting on a microscopic particle, and therefore there is no electrical ponderomotive force as defined in Section I.

The integrand in (6) is a *linear* vector function of the vector element of surface $\mathbf{dS}$. We may speak of it then as a force $\mathbf{f}_e$ acting on $|\mathbf{dS}|$ which is derivable from a tensor, Maxwell's symmetric stress tensor for empty space.

IV. The Mechanical Stress Tensor?—How shall we now define the electrical ponderomotive force within continuous matter? It would seem that again the definition should be through the failure of ordinary mechanics. Presumably, in an electric field, the completely recognizable mechanical forces acting on any arbitrarily chosen continuous volume within the body will not balance according to the mechanics of continuous bodies, and we must invoke a volume electrical force $\mathbf{F}_e$ which we thereby define to restore this balance.

But what are these completely recognizable mechanical forces? In the mechanics of continuous bodies in the absence of electromagnetic fields, it is asserted that in addition to gravitational or inertial volume forces, there is acting on each element of the bounding surface, $\mathbf{dS}$, of the volume, a force, $-\mathbf{f}_m|\mathbf{dS}|$ impressed by the contiguous matter,[1] and that this system of forces is derivable from a mechanical stress tensor, which is a function of the strains in the material. From the way this stress tensor is used in deriving the equations of mechanics, we may conclude that a meaningful operational definition of these mechanical forces is as follows.

Make a physical cut in the material along an element of surface. Introduce means for keeping the strains in the material on both sides of the cut the same as they were before the cut was made. Then the force introduced by these means is the force $-\mathbf{f}_m|\mathbf{dS}|$.

It is not assumed that the cut and the introduced means do not disturb the microstructure and micromechanics of the material. For example, in the case of a fluid the cut and means would cause molecules to be reflected which would otherwise pass through the geometric element of surface $\mathbf{dS}$. It is assumed, however, that in spite of the change in the micromechanics, there is no change in the observable macromechanics.

Now in the case that there is an electric field, let us tentatively continue to define the mechanical forces acting on a volume within matter in the same way. Now, however, just as for the particles and isolated bodies of Section I, we must limit the means used for keeping the strains on the two sides of the cut unchanged by the cut, to such as will also leave the electric fields on the two sides of the cut unchanged. Thus, for a dielectric fluid we may use as means, piston walls or heads made of very thin sheets of perfectly insulating material. But now, as we proceed to show, we run into the dilemma that the mechanical forces $-\mathbf{f}_m|\mathbf{dS}|$ thus found are not derivable from a tensor.

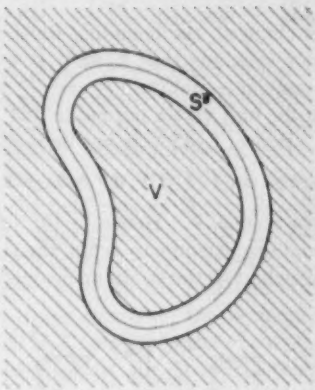

FIGURE 1

Consider a volume V, in a material, surrounded by a closed surface S^*. We now make a thin cut all along S^*, leaving a thin shell of empty space within which there will be an electric field $\mathbf{E}^*$, figure 1. If the means used for impressing the forces $-\mathbf{f}_m|\mathbf{dS}|$ do not introduce charges, then $\mathbf{E}^*$ is related to the fields $\mathbf{E}$ and $\mathbf{D}$ within the material at $\mathbf{S}^*$ by the relations

$$\mathbf{E}^* \cdot \mathbf{dS}^* = \mathbf{D} \cdot \mathbf{dS}^* \tag{7}$$

$$[\mathbf{E}^* \times \mathbf{dS}^*] = [\mathbf{E} \times \mathbf{dS}^*]. \tag{8}$$

Now the volume V, bounded by the shell of empty space along S^* is an isolated body acted on by the purely mechanical external forces $-\mathbf{f}_m|\mathbf{dS}^*|$ in the sense of Section III, and we may apply the equation (6) giving

$$\iint_{S^*} \frac{1}{8\pi} (2\mathbf{E}^*\mathbf{E}^* \cdot \mathbf{dS}^* - \mathbf{E}^{*2}\,\mathbf{dS}^*) = -\iint_{S^*} -\mathbf{f}_m|\mathbf{dS}^*| - \mathbf{F}_m \tag{9}$$

where presumably the right-hand member of (9) is the total electrical force acting on V, and $\mathbf{F}_m$ is the total volume distributed impressed mechanical force, or

$$-\mathbf{F}_m - \iint_{S^*} -\mathbf{f}_m|\mathbf{dS}^*| = \iiint_V \mathbf{F}_e\, dV \tag{10}$$

where $\mathbf{F}_e$ is the presumably uniquely determinable ponderomotive electrical force per unit volume within V.

Now, if $\mathbf{dS}$, unrelated to $\mathbf{dS^*}$, is an arbitrarily oriented element of surface within the fixed and unchanging shell of empty space, $\frac{1}{8\pi}(2\mathbf{E^*E^*}\cdot\mathbf{dS} - \mathbf{E^{*2}}\,\mathbf{dS})$ is a linear vector function of $\mathbf{dS}$. However, for the vector function of $\mathbf{dS^*}$, $\mathbf{f}_e|\mathbf{dS^*}| = \frac{1}{8\pi}(2\mathbf{E^*E^*}\cdot\mathbf{dS^*} - \mathbf{E^{*2}}\,\mathbf{dS^*})$, as the orientation of $\mathbf{dS^*}$ is changed, the bounding walls of the cut must also change, and we may not conclude that $\mathbf{f}_e|\mathbf{dS^*}|$ is a *linear* vector function of $\mathbf{dS^*}$. In fact, applying equations (7) and (8) we see that $\mathbf{f}_e|\mathbf{dS^*}|$ is a cubic function of $\mathbf{n}$ the unit vector normal to $\mathbf{dS^*}$, and $\mathbf{dS^*}$, if $\mathbf{D}$ is not equal to $\mathbf{E}$.

Hence, $\mathbf{f}_e|\mathbf{dS^*}|$ is not derivable from a tensor and $\int\int_{S^*}\mathbf{f}_e|\mathbf{dS^*}|$ is not equal to $\int\int\int_V \mathbf{F}_e\,dV$, where $\mathbf{F}_e$ is a vector independent of the shape of the volume V. Hence, by (9) $-\mathbf{f}_m|\mathbf{dS^*}|$ is also not derivable from a tensor, and our attempt to define the mechanical stress tensor through the forces which keep the strain unchanged on making a cut, has failed.

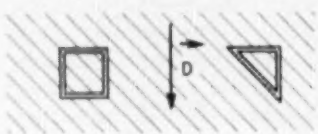

FIGURE 2

We may illustrate the foregoing development by a simple example. Consider a homogeneous dielectric material, with dielectric constant, k, very large, in a uniform field $\mathbf{D} = k\mathbf{F}$, figure 2. Consider a volume which is a unit cube with four faces parallel to $\mathbf{D}$. Surround this cube with a cut making an empty shell space. In the two faces of the cut perpendicular to $\mathbf{D}$, $\mathbf{E^*} = \mathbf{D}$. For these two faces the contribution to the component parallel to $\mathbf{D}$ of the Maxwell stress integral of (6) will be, respectively, $-\frac{1}{8\pi}\mathbf{D}^2$ and $+\frac{1}{8\pi}\mathbf{D}^2$. In the remaining four faces $\mathbf{E^*} = \mathbf{E} = \frac{1}{k}\mathbf{D}$ and is nearly zero. The component parallel to $\mathbf{D}$ of the Maxwell stress integral (9) is then zero, and therefore so also must be that component of the integral of $-\mathbf{f}_m|\mathbf{dS^*}|$ of (9) and (10).

But now consider the volume consisting of the half cube shown in figure 2 with one square face perpendicular to $\mathbf{D}$, and the other square face and the two triangular faces parallel to $\mathbf{D}$. In the cut along the square face perpendicular to $\mathbf{D}$, $\mathbf{E^*} = \mathbf{D}$, and the contribution to the component parallel to $\mathbf{D}$ of the Maxwell stress integral of (6) is $-\frac{1}{8\pi}\mathbf{D}^2$. For the three faces parallel to $\mathbf{D}$, $\mathbf{E^*}$ is nearly zero and the contribution to the Maxwell stress integral is zero. For the remaining diagonal face, $\mathbf{E^*}$ will be nearly perpendicular to the face and of magnitude $|\mathbf{D}|/\sqrt{2}$. The contribution to the component parallel to $\mathbf{D}$ of the Maxwell stress

integral is $+\frac{1}{8\pi}\mathbf{D}^2/2$. The total Maxwell stress integral will then have a component parallel to $\mathbf{D}$ of magnitude $-\frac{1}{8\pi}\mathbf{D}^2/2$, and is not zero. Thus we see that the Maxwell stress integral, and that therefore also the integral of $-\mathbf{f}_m|d\mathbf{S}^*|$ depends on the shape and orientation of the volume considered, and that therefore the forces $\mathbf{f}_m|d\mathbf{S}^*|$ are not derivable from a tensor.

V. The Surface Electrical Ponderomotive Force.—The various formulae which have been proposed for the electrical ponderomotive force in matter, in the literature of classical electromagnetism, give surface forces at the bounding surfaces of material bodies, as well as volume forces within the bodies. This is because the proposed formulae for the volume force involve space derivatives of functions of the field vectors $\mathbf{D}$ and $\mathbf{E}$, and material parameters such as density and dielectric constant. At the boundaries of bodies the field vectors $\mathbf{D}$ and $\mathbf{E}$ are generally discontinuous, and also the material parameters as density, etc. In the mathematical application of the volume ponderomotive force formulae, the bounding surface is replaced by a thin layer in which $\mathbf{D}$, $\mathbf{E}$, and the material parameters vary continuously from their values within the body to their different values just outside the boundary. Application of the volume force formulae to this thin layer then leads to a surface force formula.

The appearance of these surface electrical forces suggests that there may be a way out of the dilemma presented by the fact that the mechanical forces which must be introduced in a cut to keep the strain unchanged, are not derivable from a tensor. We may say that on making the cut, we introduce new electrical ponderomotive forces, namely the surface forces which are related to and calculable from the volume electrical forces. We may say then that the mechanical forces $-\mathbf{f}_m|d\mathbf{S}^*|$ which are introduced into the cut must compensate for the surface electrical forces as well as take the place of the contiguous material in keeping the strain what it was before the cut was made. We might expect that after allowing for the surface electrical force, $\mathbf{f}_e|d\mathbf{S}^*|$, the remaining mechanical force, $(-\mathbf{f}_m + \mathbf{f}_e)|d\mathbf{S}^*|$, will be derivable from a tensor.

We are led then to a tentative circular kind of definition of the mechanical stress tensor and volume electrical ponderomotive force. The mechanical forces $-\mathbf{f}_m|d\mathbf{S}^*|$ in a cut are observed. Then the volume electrical force, $\mathbf{F}_e$ is such as leads to surface forces $\mathbf{f}_e|d\mathbf{S}^*|$ which make $(-\mathbf{f}_m + \mathbf{f}_e)|d\mathbf{S}^*|$ derivable from a tensor, and such that for any continuous volume, and bounding surface S^*,

$$\iiint_V \mathbf{F}_e\,dV + \iint_{S^*} \mathbf{f}_e|d\mathbf{S}^*| = -\iint_{S^*} -\mathbf{f}_m|d\mathbf{S}^*| - \mathbf{F}_m. \quad (11)$$

However, this does not lead to a unique electrical ponderomotive force and mechanical stress tensor.

VI. Non-uniqueness of the Electrical Ponderomotive Force and Mechanical Stress Tensor.—We may readily see that infinitely many volume electrical forces, $\mathbf{F}_e$, with related surface force $\mathbf{f}_e|\mathbf{dS}|$ may be found which will satisfy (11) and which will make $(-\mathbf{f}_m + \mathbf{f}_e)|dS^*|$ derivable from a tensor. For this we may take any tensor whose components are functions of the field vectors, $\mathbf{E}$, $\mathbf{D}$, and the scalar charge density, ρ, and material parameters, such as density or dielectric constant, and which in empty space, where $\mathbf{E} = \mathbf{D}$, and $\rho = 0$, and the material parameters reduce to the appropriate values, becomes identical with Maxwell's electrical stress tensor. Then the divergence of this tensor gives a valid electrical volume force.

Maxwell's stress tensor itself, for empty space, by equation (6) has components,

$$\mathcal{T}^M_{xx} = \frac{1}{8\pi}(\mathbf{E}_x^2 - \mathbf{E}_y^2 - \mathbf{E}_z^2)$$

$$\mathcal{T}^M_{xy} = \frac{1}{8\pi}(2\mathbf{E}_x\mathbf{E}_y) \qquad (12)$$

etc.

Now by (9) for any volume surrounded by an empty shell which follows the bounding surface S^*,

$$\iint_{S^*} T^M_{ij}\, \mathbf{dS}^*_j = -\iint_{S^*} -\mathbf{f}_{mi}|\mathbf{dS}^*| - \mathbf{F}_m \qquad (13)$$

where T^M_{ij} refers to the empty space outside S^*, and the usual summation convention for repeated subscripts is implied.

We now consider any other tensor T_{ij} which reduces to T^M_{ij} in empty space. Then of course

$$\iint_{S^*} T^{(1)}_{ij}\, \mathbf{dS}^*_j = \iint_{S^*} \mathcal{T}^M_{ij}\, \mathbf{dS}^*_j = -\iint_{S^*} \mathbf{f}_{mi}|\mathbf{dS}^*| - \mathbf{F}_m, \qquad (14)$$

where $T^{(1)}_{ij}$ refers to the values of T_{ij} outside S^*. We now apply Gauss's theorem to the first integral of (14) but take into account the fact that T_{ij} is discontinuous at S^*. We therefore have

$$\iint_{S^*} T^{(1)}_{ij}\, dS_j = \iint_{S^*} (T^{(1)}_{ij} - T^{(2)}_{ij})\, dS^*_j + \iint_{S^*} T^{(2)}_{ij}\, dS^*_j$$

$$= \iint_{S^*} (T^{(1)}_{ij} - T^{(2)}_{ij})\, dS^*_j + \iiint_V \frac{\partial T_{ij}}{\partial x_j}\, dV$$

$$= -\iint_{S^*} -\mathbf{f}_{mi}|dS^*| - \mathbf{F}_m \qquad (15)$$

where $T^{(2)}_{ij}$ refers to values of T_{ij} inside S^*.

Since T_{ij} is a tensor, $\dfrac{\partial T_{ij}}{\partial x_j}$ is the x_i component of a vector, which we shall now call the volume electric force, $\mathbf{F}_e$. $(T_{ij}^{(1)} - T_{ij}^{(2)})\, dS_j^*$ is the x_i component of a vector, if $\mathbf{dS}^*$ is fixed, and we call it the x_i component of $\mathbf{f}_e|dS^*|$, the surface electrical force related to $\mathbf{F}_e$. Then according to (15) we do have the necessary condition (11).

Furthermore, since V is an arbitrary volume, it follows that $(-\mathbf{f}_m + \mathbf{f}_e)|\mathbf{dS}^*|$ is derivable from a tensor which we call the mechanical stress tensor, M_{ij}.

The non-uniqueness of the electrical and mechanical stress tensors, T_{ij} and M_{ij}, is evident from the method of their derivation. We may see directly, however, that they are not unique in their validity as follows. Let R_{ij} be any tensor function of the electrical field variables, the strain variables, and the electrical and mechanical parameters which we may choose to characterize the matter being examined. Then we may take as also valid electrical and mechanical stress tensors, $T'_{ij} = T_{ij} + R_{ij}$ and $M'_{ij} = M_{ij} - R_{ij}$. Since any experiment which can be performed can only determine the net force on a total body, or the net force applied to an external surface, and since these net forces are completely determinable from the sum of the two tensors, $T_{ij} + M_{ij}$, and since $T'_{ij} + M'_{ij} = T_{ij} + M_{ij}$, no experiment can distinguish between the validities of T'_{ij}, M'_{ij}, and T_{ij}, M_{ij}.

Throughout the literature of the subject, the electrical volume ponderomotive force is assumed to have unique meaning, although a meaningful operational definition is not given. One universal formula offered[2] is

$$\mathbf{F}_e = E(\rho + \rho') = \mathbf{E}\left(\frac{1}{4\pi}\,\mathrm{div}\,\mathbf{D} - \mathrm{div}\,\mathrm{P}\right) = \frac{1}{4\pi}\,\mathbf{E}\,\mathrm{div}\,\mathbf{E}, \quad (16)$$

where $\mathbf{P}$ is the polarization vector

Since

$$\iiint_V \frac{1}{4\pi}\,\mathbf{E}\,\mathrm{div}\,\mathbf{E}\,dV = \frac{1}{8\pi}\iint_S (2\mathbf{E}\mathbf{E}\cdot\mathbf{dS} - \mathbf{E}^2\,\mathbf{dS}) \quad (17)$$

we see that we have here one of the possible but not uniquely valid formulae as described in Section VI.

Another universal formula[3] is

$$\iiint_V \mathbf{F}_e\,dV = \iiint_V \mathbf{P}\cdot\nabla\mathbf{E}\,dV = \frac{1}{8\pi}\iint_S 2\mathbf{E}\mathbf{D}\cdot\mathbf{dS} - \mathbf{E}^2\,\mathbf{dS} \quad (18)$$

again giving a tensor which agrees with Maxwell's in empty space.

For the special case of a material which has a dielectric constant, k, which is a function only of the density, τ, the formula

$$\mathbf{F}_s = \frac{1}{8\pi}\left(-\mathbf{E}^2 \operatorname{grad} k + \operatorname{grad} \mathbf{E}^2 \tau \frac{dk}{d\tau}\right) \tag{19}$$

is frequently given.[4] Again we have that (19) reduces to

$$\iiint_V \mathbf{F}_s\, dV = \frac{1}{8\pi} \iint_S 2\mathbf{E}\mathbf{D}\cdot d\mathbf{S} - \left(\mathbf{E}\cdot\mathbf{D} - \mathbf{E}^2\tau\frac{dk}{d\tau}\right) d\mathbf{S} \tag{20}$$

and again on the right of (20) we have a tensor which reduces to Maxwell's stress tensor in empty space where $\mathbf{D} = \mathbf{E}$, and $\tau = 0$.

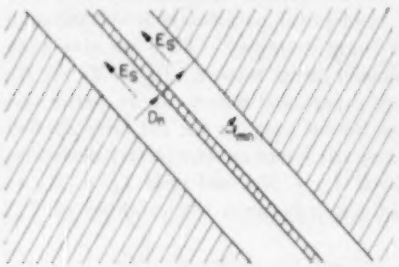

FIGURE 3

Expressions such as (19) are often derived[4] by assuming the existence of an energy density function, u, and equating the increase in the energy of a system, to the work done by applied force in a change of strain. It is clear, however, from the foregoing, that only net forces can be so determined, and that the designation of electrical parts and mechanical parts of such net forces is without meaning.

VII. The Net Stress Tensor and Energy Density.—It is clear that all the information which can be verified concerning the ponderomotive forces on a medium is contained in a knowledge of the field vectors $\mathbf{E}$ and $\mathbf{D}$, and of the net force $-\mathbf{f}_m|dS|$ at a cut, for all orientations of the cut, and at all points in the medium.

From equation (10) modified to include the application of net externally applied volume forces $\mathbf{F}$, we have

$$\iint_{S^*} -\frac{1}{8\pi}\left(2\mathbf{E}^*\mathbf{E}^*\cdot d\mathbf{S}^* - \mathbf{E}^{*2} d\mathbf{S}^*\right) + \mathbf{f}_m|dS^*| = \iiint_V \mathbf{F}\, dV. \tag{21}$$

It follows then that the integrand on the left of (21) defines a tensor which we call the net stress tensor.

If the matter in question has an electromechanical energy density function, u, then $\mathbf{f}_m$ and the net stress tensor may be determined therefrom, but they also have meaning independently of the existence of such a function.

As an example, take the case where there is an energy density u, which is a function of the electric field, $\mathbf{E}$, or $\mathbf{D}$, and the material density, τ, only.

Referring to figure 3, consider a cut, and in the cut, place a thin slab of material, subject to the same set of surface forces $-\mathbf{f}_m|dS|$ as the sides of the cut. Then in this slab, the field vectors, $\mathbf{E}$ and $\mathbf{D}$, are the same as in the neighboring material.

Now give the slab a shear, slipping the one surface of the slab parallel to the other. Since the volume of the slab, and therefore also its density, and since also the field vectors are unchanged, then the energy of the slab is unchanged. The surface forces $\mathbf{f}_m$, therefore, do no work, during this shear, and therefore the force component parallel to the surface, $\mathbf{f}_{m_s}$, is zero.

$$\mathbf{f}_{m_s} = 0. \tag{22}$$

Now let the slab be expanded, by motion of its sides in the normal direction so that its volume per unit area is increased by ΔV. The increase in energy within the slab per unit area will be,

$$\begin{aligned}\Delta(uV) = V\Delta u + u\Delta V &= V\left(\frac{\partial u}{\partial \tau}\right)_{E_s, D_n}\frac{\Delta\tau}{\Delta V}\Delta V + u\Delta V \\ &= \left(-\tau\left(\frac{\partial u}{\partial \tau}\right)_{E_s, D_n} + u\right)\Delta V\end{aligned} \tag{23}$$

where the subscripts E_s, D_n, indicate that E_s and D_n are to be kept constant during the differentiation of u with respect to τ.

The increase of energy per unit area in the empty space of the cut will be $-\frac{1}{8\pi}(E_s^2 + D_n^2)\,\Delta V$.

$\mathbf{D}_s$ in the slab will be changed by the change in τ, and there will be energy per unit area of the cut supplied through the electric field given by

$$\frac{1}{4\pi}\mathbf{E}_s\cdot\Big(V\Delta\mathbf{D}_s + [\mathbf{D}_s - \mathbf{E}_s]\Big)\Delta V = \frac{1}{4\pi}\left(-\tau\left[\frac{\partial D_s}{\partial \tau}\right]_{E_s, D_n} + \mathbf{D}_s - \mathbf{E}_s\right)\Delta V \tag{24}$$

where of course, $\mathbf{D}_s$ is related to $\mathbf{E}_s$, $\mathbf{D}_n$, and τ by

$$\mathbf{E}_s = 4\pi\frac{\partial}{\partial D_s}(u[\mathbf{D}_s, \mathbf{D}_n, \tau]). \tag{25}$$

Equating the increase of slab energy (23) minus the loss of energy in the empty space, $\frac{1}{8\pi}(\mathbf{E}_s^2 + \mathbf{D}_n^2)\,\Delta V$ to the sum of the energy supplied electrically (24) and the work done mechanically, or $-\mathbf{f}_{m_s}\Delta V$, we have

$$\left(-\mathbf{f}_{ms} - \frac{1}{4\pi}\tau\mathbf{E}_s\left[\frac{\partial \mathbf{D}_s}{\partial \tau}\right]_{E_s,\ D_n} + \frac{1}{4\pi}\mathbf{E}_s\mathbf{D}_s - \frac{1}{4\pi}\mathbf{E}_s^2\right)\Delta V =$$

$$\left[\left(-\tau\left[\frac{\partial u}{\partial \tau}\right]_{E_s,\ D_n} + u\right) - \frac{1}{8\pi}(\mathbf{E}_s^2 + \mathbf{D}_n^2)\right]\Delta V. \quad (26)$$

This, then, gives us

$$\mathbf{f}_{ms} = +\tau\left(\frac{\partial u}{\partial \tau}\right)_{E_s,\ D_n} - u - \frac{1}{4\pi}\tau\mathbf{E}_s\left[\frac{\partial \mathbf{D}_s}{\partial \tau}\right]_{E_s,\ D_n} +$$

$$\frac{1}{8\pi}(\mathbf{D}_n^2 - \mathbf{E}_s^2 + 2\mathbf{E}_s\mathbf{D}_n). \quad (27)$$

To get the *net* mechanical volume force, **F**, which must be introduced to hold a given volume, V, within the medium in equilibrium, we then have (21) which we rewrite as

$$\int\int\int_V \mathbf{F}\,dV = -\int\int_{S^*}\frac{1}{4\pi}\,\mathbf{E}\mathbf{D}\cdot d\mathbf{S}^* + \frac{1}{8\pi}\,(\mathbf{D}_n^2 - \mathbf{E}_s^2 -$$

$$2\mathbf{E}_s\mathbf{D}_n)d\mathbf{S}^* - \mathbf{f}_{ms}d\mathbf{S}^* \quad (28)$$

Let us further specialize u to be of the form

$$u = \frac{1}{8\pi}k(\tau)\mathbf{E}^2 + W(\tau) = \frac{1}{8\pi}\left(k\mathbf{E}_s^2 + \frac{1}{k}\mathbf{D}_n^2\right) + W = \frac{1}{8\pi}\mathbf{E}\cdot\mathbf{D} + W. \quad (29)$$

Then

$$\tau\left(\frac{\partial u}{\partial \tau}\right)_{E_s,\ D_n} = \frac{1}{8\pi}\left(\mathbf{E}_s^2 - \frac{1}{k^2}\mathbf{D}_n^2\right)\tau\frac{dk}{d\tau} + \tau\frac{dW}{d\tau} = \frac{1}{8\pi}(\mathbf{E}_s^2 - \mathbf{E}_n^2)\,\tau\frac{dk}{d\tau} +$$

$$\tau\frac{dW}{d\tau} \quad (30)$$

and

$$\tau\left(\frac{\partial \mathbf{D}_s}{\partial \tau}\right)_{D_n,\ E_s} = \tau\frac{\partial}{\partial \tau}(k\mathbf{E}_s) = \mathbf{E}_s\,\tau\frac{dk}{d\tau}. \quad (31)$$

Substituting (31) and (30) into (27)

$$\mathbf{f}_{ms} = -\frac{1}{8\pi}\mathbf{E}^2\,\tau\frac{dk}{d\tau} + \tau\frac{dW}{d\tau} - W + \frac{1}{8\pi}(\mathbf{E}_s\mathbf{D}_s - \mathbf{E}_n\mathbf{D}_n - \mathbf{E}_s^2 + \mathbf{D}_n^2). \quad (32)$$

Substituting into (28)

$$-\int\int\int_V \mathbf{F}\,dV = \int\int_S \frac{1}{8\pi}\,(2\mathbf{ED}\cdot d\mathbf{S}^* - \mathbf{E}\cdot\mathbf{D}\,d\mathbf{S}^*) + \left(\frac{1}{8\pi}\mathbf{E}^2\,\tau\,\frac{dk}{d\tau} - \tau\,\frac{dW}{d\tau} + W\right)d\mathbf{S}^*. \quad (33)$$

The integrand on the right of (33) is now a linear vector function of $d\mathbf{S}^*$, and defines a tensor, the negative of the net stress tensor. If we apply Gauss's theorem, we get

$$-\mathbf{F} = \rho\mathbf{E} - \frac{1}{8\pi}\mathbf{E}^2\,\text{grad}\,k + \text{grad}\,\frac{1}{8\pi}\mathbf{E}^2\,\tau\,\frac{dk}{d\tau} + \text{grad}\left(W - \tau\,\frac{dW}{d\tau}\right) \quad (34)$$

where $\rho = \frac{1}{4\pi}\,\text{div}\,\mathbf{D}$.

Equation (34) gives the negative of the net volume force which is impressed on the material to hold it in equilibrium. In various places, the first term, the sum of the first two terms and the sum of the first three terms are designated, respectively, as the electric volume force.

[1] In subsequent integrations over a closed surface enclosing matter, the direction of $d\mathbf{S}$ will be that of the outer normal. This is the reason for the negative sign used here.

[2] Richardson, *The Electron Theory of Matter*, Cambridge University Press, p. 206, 1914.

[3] Page and Adams, *Principles of Electricity*, D. Van Nostrand, New York, 15th Printing, pp. 45–49.

[4] Stratton's *Electromagnetic Theory*, McGraw-Hill, 1941, p. 139. A number of early references are given on pp. 145 and 150.

INFRA-RED BANDS IN THE SPECTRUM OF NH_3

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Measurements made in this laboratory attempting to establish whether or not ammonia was a component of the earth's atmosphere required the remeasurement in the laboratory of the fundamental bands in the ammonia spectrum. It was found, notably in the bands ν_2 and ν_4, that the spectra were appreciably better resolved than in earlier attempts and it has therefore seemed of interest to look at these again with some care. Measure-

ments have been completed on the four fundamental bands and as well on the low frequency difference band originating with molecules in the excited state $\nu_2(1^-)$ making a transition to the state $2\nu_2(2^+)$. A portion of this band had been seen earlier by Sheng, Barker and Dennison,[1] but an interesting portion of the band was hidden by the intense carbon dioxide fundamental band overlapping this region. A certain amount of water vapor falsification was also noted in this region. It has seemed desirable to make a preliminary report on these measurements at this time because it will demand considerable time to complete the calculations on the molecular constants which these data seem to warrant.

The measurements were made in all cases, except on the 10 μ band, using a vacuum grating spectrograph described elsewhere[2] so that the falsifying effects due to water vapor and carbon dioxide could be eliminated. The samples of gas were also carefully dried. One method which proved

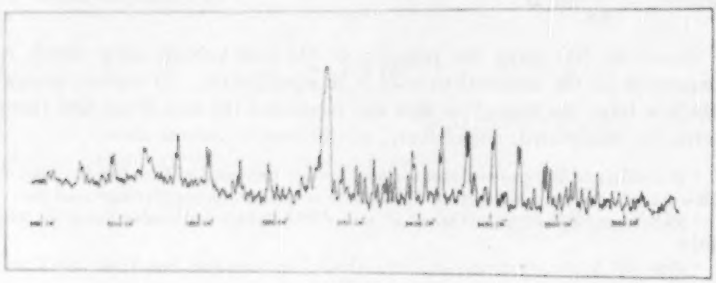

FIGURE 1

ν_4 in the infra-red spectrum of NH_3.

particularly efficacious was to place a small amount of magnesium nitride in the absorption cell, any residual water vapor which might be present being thus absorbed and NH_3 being liberated according to the reaction $6H_2O + Mg_3N_2 \rightarrow 2NH_3 + 3Mg(OH)_2$.

Figure 1 shows the absorption pattern of the perpendicular band ν_4 studied first by Barker.[3] Our pattern verifies in general that shown by Barker. Narrower slits could be used in our experiment because the effects of atmospheric water vapor could be eliminated and considerably better resolution has been achieved. The pattern of Barker could substantially be obtained by operating our spectrometer with somewhat widened slits. A complete analysis of this band has not been made although many of the characteristics which are to be expected have been spotted. This region was studied using an echellette replica grating with 3600 lines per inch and with effective slit widths less than 0.5 cm.$^{-1}$.

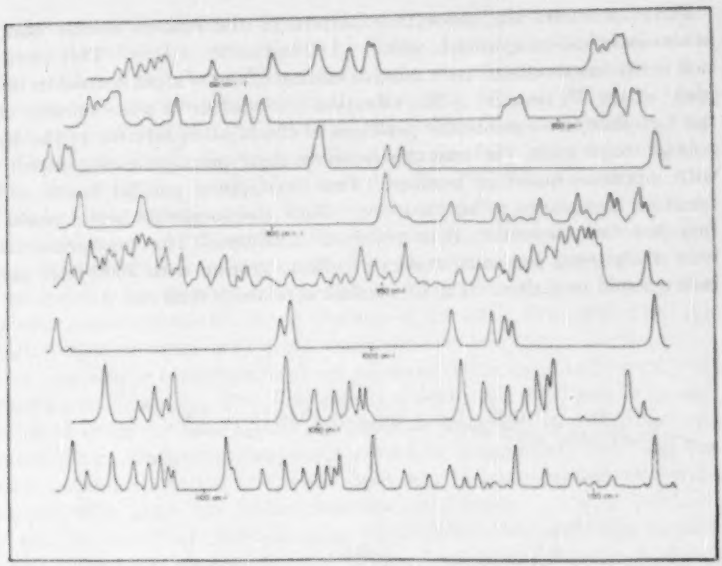

FIGURE 2

Transitions ν_2 $(0^- \rightarrow 1^+)$ and ν_2 $(0^+ \rightarrow 1^-)$ in the infra-red spectrum of NH_3.

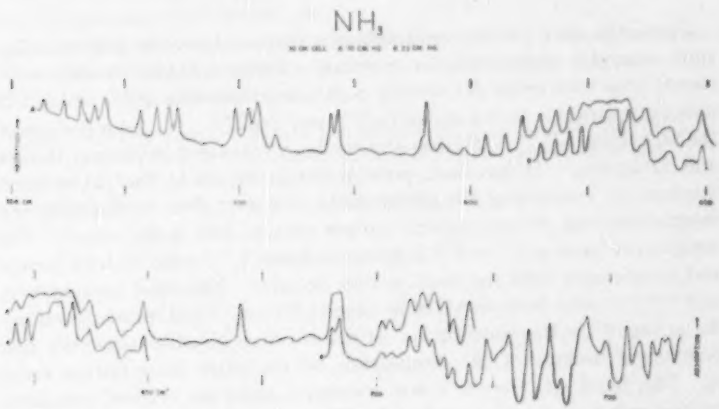

FIGURE 3

The transition ν_2 $(1^- \rightarrow 2^+)$ in the infra-red spectrum of NH_3.

Figure 2 shows the absorption pattern of the famous double band in ammonia known as ν_2 (i.e., $\nu_2(0^- \rightarrow 1^+)$ and $\nu_2(0^+ \rightarrow 1^-)$). This vibration is the one simulated by a relative motion of the N atom normal to the plane of the H_3 triangle. The vibration levels occur in pairs because of the fact that two equilibrium positions of the N atom relative to the H_3 triangle must exist, the intervals between these pairs increasing rapidly with vibration quantum number. Two overlapping parallel bands will result for this reason rather than one. Here also somewhat better resolution has been achieved than reported elsewhere. The measurements were made using the same replica echellette grating with 3600 lines per inch referred to earlier. The slit widths were about 0.25 cm.$^{-1}$.

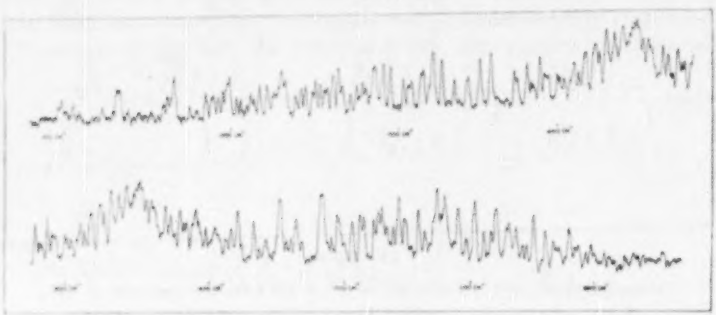

FIGURE 4

ν_1 and ν_3 in the infra-red spectrum of NH_3.

Evidently since the intervals between pairs of levels in this vibration state intervals with vibration quantum number a similar double band should arise with molecules already populating the states $\nu_2(1^+)$ and $\nu_2(1^-)$ making transitions to the states $2\nu_2(2^-)$ and $2\nu_2(2^+)$. Indeed a portion of the transition $\nu_2(1^- \rightarrow 2^+)$ has already been measured by Sheng, Barker and Dennison.[1] It has been possible for us to study the entire band because, by evacuating the spectrograph, we were able to eliminate the interference due to atmospheric carbon dioxide and water vapor. The component band $\nu_2(1^- \rightarrow 2^+)$ is shown in figure 3. At the high frequency end interference with the band ν_3 may be seen. The other components, $\nu_2(1^+ \rightarrow 2^-)$, may be expected to lie close to 970 cm.$^{-1}$ and would, therefore, lie on top of the fundamental ν_3. It has not been possible to identify this component because of the interference by the much more intense band ν_3. The band $\nu_2(1^+ \rightarrow 2^-)$ was measured using an original echellette grating ruled at the University of Michigan by Barker with 1200 lines per inch. No separations less than about 1 cm.$^{-1}$ were observed.

The two bands shown in figures 2 and 3 are probably the ones of most immediate interest. As suggested by Sheng, Barker and Dennison, each J transition in the P and R branches is split into its K-components. The P branch of the low frequency component of ν_2 (i.e., $\nu_2(0^- \rightarrow 1^+)$) has been resolved sufficiently so that all the components may be seen. As indicated by Sheng, Barker and Dennison the $P(1)$ line is absent, the $P(2)$ line is double, the $P(3)$ line is double, the $P(4)$ line is quadruple, the $P(5)$ line is quadruple, etc. This may be seen to be the case in figure 2. Similarly it may be shown that the $R(0)$ and $R(1)$ lines should be single, the $R(2)$ and $R(3)$ lines, triple, the $R(5)$ and $R(6)$ lines, quintuplets, etc. Our spectrogram shows the $R(1)$, $R(3)$ and $R(5)$ lines to have the number of components predicted, but in the case of the $R(2)$, $R(4)$, $R(6)$ lines the high frequency component is not resolved.

A comparable resolution has been achieved in the band $\nu_3(1^- \rightarrow 2^+)$ to that obtained for ν_2. The $P(1)$ line is absent; the $P(2)$ line is an unresolved doublet; the $P(3)$ line is double as predicted; the $P(4)$ line appears triple, the fourth component remaining unresolved; etc. On the high frequency side the first few R lines may be distinguished, but overlapping with ν_2 quickly makes identification difficult.

For the sake of completeness figure 4 is included which shows the parallel band ν_1 and the overlapping band ν_3. It is essentially like the work reported by Hardy and Dennison[4] except that some of the details of the perpendicular band are different, probably because the falsification due to water vapor could here be eliminated.

A more complete discussion of this work will be published elsewhere when the calculations on the data have been completed and a more complete analysis has been carried out.

The authors wish to express their gratefulness to The National Research Council and to The Research Corporation in New York for Grants-in-Aid which have facilitated this work.

[1] Sheng, Hsi-Yin, Barker, E. F., and Dennison, D. M., *Phys. Rev.*, **60**, 786 (1941).
[2] Bell, E. E., Noble, R. H., and Nielsen, H. H., *Rev. Sci. Instruments*, **18**, 48 (1947).
[3] Barker, E. F., *Phys. Rev.*, **55**, 657 (1939).
[4] Dennison, D. M., and Hardy, J. D., *Ibid.*, **39**, 938 (1932).

NATIONAL ACADEMY OF SCIENCES CONFERENCE ON THE ULTRACENTRIFUGE*

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Communicated May 26, 1950

On June 13–16, 1949, a conference on the ultracentrifuge, sponsored by the National Academy of Sciences and organized by D. A. MacInnes, was held at the Ram's Head Inn, Shelter Island, New York. The participants were W. J. Archibald, J. W. Beams, P. Ecker, L. J. Gosting, H. S. Harned, C. W. Hiatt, W. Kauzmann, G. Kegeles, L. G. Longsworth, D. A. MacInnes, T. L. McMeekin, D. H. Moore, J. L. Oncley, B. B. Owen, K. O. Pedersen, M. L. Randolph, T. Shedlovsky, R. Trambarulo, M. Wales, and J. W. Williams.

The following is a brief account of the topics that were discussed at the conference. It is hoped that this report will serve to bring to the attention of all workers in the field some of the outstanding problems of the ultracentrifuge and to stimulate efforts toward their solution. As reporter for the conference the author submitted a preliminary draft of this manuscript to the participants and gratefully acknowledges their generous cooperation in the correction of errors, and the suggestion of the many revisions that are incorporated in the following account.

Introduction.—The discussion at the conference on the ultracentrifuge was organized, in large measure, around each of the terms that appear in the expression for the determination of molecular weight with the aid of the sedimentation velocity method.[1] In this expression, which is:

$$M = \frac{RTs}{D(1 - \rho v)} \tag{1}$$

s is the sedimentation velocity, D the diffusion coefficient, v the partial specific volume of the material being studied and ρ the density of the solution. The meaning and experimental evaluation of each of these quantities were considered, as well as the temperature, T, of the measurements. Only the gas constant, R, was taken for granted.

Although the principal use of the ultracentrifuge has been in the determination of the molecular weight and homogeneity of proteins an attempt was made to avoid too much discussion of the many problems connected with proteins as such. Thus in the session devoted to diffusion, and again in the one concerned with density and partial specific volume, considerable reference to work on salts was made since these materials have been used in testing and improving the experimental procedures. A most profitable period was devoted to a consideration of the problems that are peculiar to

the equilibrium ultracentrifuge. In the consideration of the sedimentation constant much of the discussion centered around centrifuge design since it is in the construction of high-speed machines capable of sedimenting small molecules that the serious engineering problems arise.

Centrifuge Design and the Sedimentation Constant.—The discussion of the relative merits of the contemporary air-, oil- and motor-driven[2] centrifuges was overshadowed by the glimpses of the centrifuges of the future given by J. W. Beams.[3] Magnetically supported and driven, the rotors of these machines spin about a vertical axis in sealed containers that permit the attainment and preservation of the best vacuum possible. Consequently the frictional losses are so low that the rotor can be kept, with negligible temperature change, in synchronism with a crystal-controlled rotating magnetic field. Owing to the radial symmetry of both the supporting magnetic field and the steel core of the rotor on which it acts, heating effects from this source are also negligible. Although the supporting field stabilizes the rotor axis on the magnetic axis with respect to radial displacements, automatic compensation for vertical displacements is achieved by feed-back control of the current through the supporting coil with the aid of a small secondary winding, placed beneath the rotor, whose inductance is influenced by the proximity of that body.

The most serious problem in connection with these machines, for which an entirely satisfactory solution has not yet been obtained, is that of acceleration without excessive heating of the rotor. In order to accelerate, some slippage between this element and the rotating field must occur and this lack of synchronism results in the generation of heat that can be dissipated from the rotor only by radiation. Work is in progress directed toward the solution of this problem.

Research at the University of Virginia has also included preliminary tests of an interference method for the detection and recording of refractive index changes in the centrifuge cell. As in the Michelson and Mach-Zehnder interferometer a beam of collimated light is split with the aid of a half-silvered mirror, one beam being passed through the centrifuge cell, the other through the reference cell at the opposite end of the rotor diameter, and the two beams then recombined before entering a telescope focused on the cells. In order to have interfering rays pass through levels in the two cells that are equidistant from the axis of rotation it is necessary to reverse the direction of one of the beams. Otherwise the ray through the top of one cell interferes with that through the bottom of the other cell. Moreover, in the absence of a synchronized shutter the alternate passage of both cells through each beam leads to the superposition of a reversed fringe pattern upon the one that is obtained with the centrifuge and reference cells interchanged.

The sensitivity of the interference method has served to focus attention

upon the distortion of the cells that occurs at high speeds. Owing to its high compression strength, crystal quartz is used for the windows, and the faces of both these and the quartz cell body are ground to a flatness of $^{2}/_{10}$ wave prior to being cemented together. Although an assembled cell is "floated" in the rotor in a thin Lucite sleeve the fringes are distorted at high speeds even with solvent in both cells. This observation emphasizes the difficulties of building cells that will have a common distortion under large stresses. As will be noted later in this report many of these difficulties disappear at the lower speeds that are characteristic of the equilibrium ultracentrifuge.

Although it is probable that the magnetically supported and driven centrifuge will eventually supplant contemporary instruments, development of the oil- and air-driven machines continues. In the case of the air-driven type, Beams' method of controlling the rotor speed has proved to be quite effective. In this method[4] an armature is attached to the driving rotor that, together with its field circuit, absorbs the excess driving energy as the speed approaches the resonance frequency of that circuit. Moreover, progress in the solution of the problem of measuring the rotor temperature *in situ* with the aid of thermistors was reported by Hiatt and Ecker.[5]

Resolving Power.—In the conventional sedimentation velocity method the resolving power of the instrument depends, in part, on the radial depth of the cell, and the strength of the rotor materials places restrictions on this depth. In the case of a mixture of two proteins of similar sedimentation constant, for example, where both would be thrown to the bottom of the cell before appreciable separation occurred, resolution can still be achieved if the proteins can be made to sediment (*a*) against a countercurrent of solution moving toward the axis of rotation or (*b*) against electric migration in the same direction. Progress with the migration procedure was reported by Randolph, who started this work at Virginia but is now carrying it forward at Tulane. Moreover, the experience gained in the construction of the multi-channelled centrifuge cells that are required in this work will doubtless prove of value in the development of such cells for use with the interference optical methods requiring a reference channel near that in which sedimentation occurs.

Diffusion.—The discussion, at the conference, of methods for the determination of diffusion coefficients served a dual purpose. Not only is a knowledge of D essential for a determination of M, equation 1, by the sedimentation velocity method but it also appears that the interferometric optical methods that are being adapted for diffusion studies will also find an application in centrifuge work. In fact progress in this direction may be most rapid if the various optical arrangements are tested on the concentration gradients that arise in diffusion before the mechanically difficult adaptation to the centrifuge is attempted.

Until recently the Lamm scale method has been almost universally used for the measurement of the refractive index gradients that arise in the free diffusion of proteins and related materials. The recent adaptation of the Gouy[6] and of the Rayleigh fringes to diffusion studies indicates, however, the trend to interference methods for this purpose. Although the optical methods are applicable to either electrolytes or non-electrolytes, in the case of dilute salt solutions sufficient precision has not yet been achieved to permit direct comparison with diffusion coefficients computed from electric mobilities with the aid of the Onsager-Fuoss theory. Using a conductance method the recent work of Harned[7] and the Yale group has, however, provided us with this essential control. Although not applicable to proteins the validity of their method has been indicated by the agreement that is obtained with the theory in the case of dilute solutions of, for example, potassium chloride. Moreover, in the case of more concentrated solutions of this salt the agreement between the results with the conductance method and those obtained by Gosting at the Rockefeller Institute with the Gouy method validates, in turn, this optical procedure.

In spite of its inherent precision the Gouy method has the limitation that the theory is restricted to the diffusion of an ideal solute, or to a mixture of such solutes, and that the fringes indicate the magnitude of the gradients in the diffusion channel but not their positions. Without abandoning this method investigators are, nevertheless, exploring the possibilities of other interference methods. Thus the adaptation of the Rayleigh fringes suggested by Philpot and Cook[8] holds promise if satisfactorily corrected cylinder lenses can be obtained. In common with the more conventional interference methods this gives the refractive index as a function of the height in the diffusion column.

It is well to bear in mind, however, that, in contrast with conventional interferometry, a layer of solution in the diffusing boundary deflects the ray as well as retarding it. If errors from this source are to be minimized compensation for the deflection should be achieved before the ray is allowed to interfere with that through the reference channel. Moreover, in the case of the Rayleigh fringes, if the resolving power of the photographic emulsion is not to be a limiting factor and if enlargement of the fringe system is to be avoided, lenses of rather long focal length are required. The objective of most investigators in this field is the development of an optical method, probably an interferometric one, that will give both the refractive index and its gradient as a function of the height in the diffusing boundary.

Diffusion of Proteins.—Owing to the presence of neutral and buffer salts and to uncertainty as to homogeneity the study of protein diffusion is a more difficult problem than that of low molecular weight substances. In order to minimize charge effects the protein is usually examined with a

buffered salt solution at the isoelectric pH of the protein as "solvent." Thus the system contains a minimum of two solutes. Since solution and solvent are prepared by dialysis of one against the other the constancy of the chemical potential of the dialyzable component across the initial boundary is thereby assured. It is not obvious, however, that this constancy is preserved as the protein diffuses and precise work may reveal coupling of the salt and protein transport processes. Moreover, with a substance whose diffusion coefficient is concentration dependent it is essential that the "solvent" contain the solute at a concentration only slightly less than that of the underlying solution, at least if the treatment of the optical data assumes ideal diffusion. Although the coefficients of most proteins do not change rapidly with the concentration Pedersen reported that even for these materials the use, at Upsala, of differential diffusion had improved materially the reproducibility of the measurements.

As was emphasized by Kegeles when two solutes are present greater care must be exercised in the manipulation of the solution than in the case of a single solute. For example, with a single solute a change of concentration due to evaporation, say, produces a much less serious error than in the case of a protein dissolved in a buffer solution where such evaporation would introduce, across the initial boundary, a gradient of chemical potential for the salt in addition to that for the protein.

Density and Specific Volume.—In the centrifuge equation, equation 1, the density volume product, ρv, has a value of approximately 0.75 for many proteins. This product is, however, subtracted from unity and if the term in parentheses is to have the same precision as s and D, ρv should be known with a precision three times as great.

In spite of the fact that pycnometer methods have long been considered as adequate for the determination of density, MacInnes has recently developed further for this purpose the float method of Lamb and Lee[9] in which the third and fourth decimals in the weight of solution displaced by a 60-ml. float are determined magnetically. Although applied thus far only to salt solutions it combines speed with an uncertainty in ρ of a very few parts per million and may facilitate the evaluation of the partial specific volume term in the case of proteins.

Although little difficulty is experienced in the determination of the density, ρ, of the solution with the desired accuracy, at atmospheric pressure at least, this is not true of the partial specific volume v since here a knowledge of the protein concentration is required. The uncertainties that limit the precision of v are not only in the measurement of solution densities but in the determination of concentration, i.e., uncertainty as to the homogeneity and reproducibility of the protein and lack of knowledge as to the moisture content of the sample or the nitrogen factor if the solution is analyzed by the micro-Kjeldahl method. The recent observation

by McMeekin[10] that the volumes of many proteins are the sums of the volumes of their amino acid constituents should serve as a useful guide in this work as the compositions of additional proteins become available.

Following considerable discussion of the question it was finally agreed that, in the equilibrium method at least, the density, ρ, is that of the solution in which the particle is suspended, not the density of the solvent, and that v is the partial, and not the apparent, volume of the protein. In the case of the sedimentation velocity method, on the other hand, the only safe procedure appears to be that used in Upsala in which the values of s, D, and v, equation 1, are extrapolated to zero concentration of the protein after correction of s and D for the viscosity effects due to the non-sedimenting solutes. The density, ρ, is then that of the pure solvent at the temperature, T, account being taken of the pressures in the cell. The necessity for this procedure arises from the probability that at finite concentrations the value of the friction coefficient in sedimentation is not identical with its value in diffusion. The need for theory and techniques that will render the extrapolations unnecessary is clear.

It is also easy to overlook the fact that the pressures in a centrifuge cell spinning at 1000 r.p.s. are not the atmospheric pressures at which ρ and v are actually measured. We were cautioned in this regard by the report of Trambarulo and Owen.[11]

With the aid of twin piezometers of 600 ml. capacity they have determined the compressibility of solutions of bovine serum albumin at pressures up to 500 bars and at protein concentrations up to 2.5%. The compressibilities of the solvent, a 0.1 normal sodium acetate buffer at the isoelectric pH, 4.73, of the albumin were also measured. Although the specific volume of the albumin decreases slightly with increasing pressure the predominant effect is that of the pressure at different levels in the centrifuge cell upon the density of the solution. For example, in a rotor spinning at 1000 r.p.s. where the pressure at the meniscus, $r_1 = 5.7$ cms., is 60 bars and that at the bottom, $r_2 = 7.3$ cms., is 470 bars, the solution at the bottom is some 0.016 g./ml. more dense than that at the top.[12] The corresponding variation in $(1-\rho v)$ would be about 6%. In this extreme case, and in the absence of compensating effects from the pressure variation of other terms in equation 1, the sedimentation constant might be expected to decrease by this amount as the boundary moved through the cell. Much larger pressure effects should be observed with some of the commonly used non-aqueous solvents, and the importance of correcting for them is emphasized by the work of Mosimann and Signer.[13] However, at the relatively low speeds, 100 r.p.s. and less, and in the short cells that characterize the equilibrium centrifuge the pressure effects should be quite negligible, even in the case of most organic solvents.

Although not on the agenda it was inevitable that the question of protein

purity should arise at every session. There was general agreement that the homogeneity of the protein should be checked by all available means, i.e., sedimentation velocity, electrophoresis, solubility, crystallizability, etc. Moreover, repeated mention was made of the fact that many of the accepted methods for storing protein preparations, such as lyophilization, do not adequately preserve the material. McMeekin proposed a recrystallization of the preparation immediately prior to use and all confreres agreed that improved methods of storage should be sought. Experimental evidence, from sedimentation studies, of the difficulty of preserving the widely used bovine serum albumin that is available commercially was presented by Kegeles.

Sedimentation Equilibrium.—One of the most fruitful sessions of the conference was that in which the possibilities of the equilibrium ultracentrifuge were explored. The recent work of Williams and Wales[14] at Wisconsin on the sedimentation equilibria of both fractionated and unfractionated polystyrene has shown how the polydispersity of this material can thus be characterized if correction for the departure of the solutions from ideality is made with the aid of osmotic pressure measurements. Moreover, these investigators have solved, with the aid of the La Place transformation, the theoretical problem of the distribution function and now feel that the next most essential development is an increase in the precision with which the equilibrium concentrations can be determined.

In view of the persisting uncertainty as to whether the molecular weight obtained with the aid of the ultracentrifuge is that of the hydrated or anhydrous material, attention was called to the work of Pedersen[15] and Drucker[16] on salts. Since these workers obtained, after making the necessary activity corrections, a molecular weight corresponding to the formula weight the conclusion appears reasonable that the anhydrous weight is the quantity measured, since both salt and protein ions can be presumed to be hydrated. In the case, however, of the sedimentation velocity method some ambiguity still remains if the density of the "bound" water differs from that of the solution.

Since the equilibrium centrifuge generally spins at a lower speed than in the case of sedimentation many of the engineering problems are thereby reduced. Moreover, the following suggestion of Archibald[17] may eliminate the necessity of establishing equilibrium and thus reduce the time of observation.

In the approach toward equilibrium the flux, ϕ, of solute through unit cross-section of the cell is

$$\phi = \omega^2 r s c - D \frac{\partial c}{\partial r}$$

where the first term on the right provides for the transport of material by sedimentation and the second by diffusion. At equilibrium this flux is zero for all values of the radius, r. Since solute cannot move through the ends of the cell at r_1 and r_2, the flux is also zero at these two levels at all times, i.e., even prior to the attainment of equilibrium. Thus a plot of $1/rc\ \partial c/\partial r$ against r should extrapolate to the same value, $\omega^2 s/D$, at r_1 and r_2 at any time, e.g., during the intermediate states that precede the establishment of sedimentation equilibrium. In contrast with the sedimentation velocity method the extrapolated intercept gives the value of the ratio, s/D, and hence for the computation of the molecular weight with the aid of equation 1 the only additional data required are the density, ρ, of the solution and the specific volume, v, of the protein. Unless a weight average value is adequate this method requires, as in the case of complete equilibrium, that the sedimenting material be monodisperse. Moreover, Pedersen noted that the extrapolation requires the greatest precision in the data that are most difficult to obtain, namely, the values near the meniscus and the bottom of the cell.

The foregoing procedure emphasizes the need for an optical method, such as the one described by Kegeles[18] utilizing a prismatic cell, that gives both c and $\partial c/\partial r$ as a function of r. The problem of cell shape remains, however, to be considered. In order to hasten the attainment of equilibrium it has become a general practice to take advantage of the convection that occurs in a channel of uniform cross-section. The theory provides, however, for transport by sedimentation and diffusion but not by convection. If the intermediate states are to be utilized as suggested by Archibald will it be necessary to use a sector-shaped cell as in sedimentation velocity measurements?

The adaptation of interferometry, using monochromatic light, to the equilibrium method involves optical problems peculiar to this procedure. In a sedimentation velocity experiment the solution above the boundary has essentially the same composition as that in the reference cell or channel. One thus has a known refractive index from which to count fringes. In the case of sedimentation equilibrium, however, at no level in the centrifuge cell is the refractive index identical with that in the reference cell. Even if the refractive index of the reference liquid were raised, by addition of a non-sedimenting solute, to a value corresponding to that at some level in the sedimentation cell this level could not be identified, except possibly by the use of white light. In view of the extreme precision that must be achieved in the determination of c and $\partial c/\partial r$ in the intermediate and equilibrium states it appears essential to continue the development of interference methods.

* The substance of this report was presented orally by Mr. D. A. MacInnes to the Academy at the Scientific Session of October 26, 1949.

[1] Svedberg, T., and Pedersen, K. O., *The Ultracentrifuge*, Oxford University Press (1940). Johnston, J. P., and Ogston, A. G., *Trans. Faraday Soc.*, **42**, 789–799 (1946). Cecil, R., and Ogston, A. G., *Biochem. J.*, **43**, 592–598 (1948).

[2] A description of the Spinco ultracentrifuge is given by Smith, E. L., Brown, D. M., Fishman, J. B., and Wilhelmi, A. E., *J. Biol. Chem.*, **177**, 305–310 (1949).

[3] Recently published work of this laboratory: Beams, J. W., *J. Applied Phys.*, **8**, 795 (1937); *Rev. Mod. Phys.*, **10**, 245 (1938). Beams, J. W., Linke, F. W., and Sommer, P., *Rev. Sci. Inst.*, **9**, 248–252 (1938). Skarstrom, C., and Beams, J. W., *Ibid.*, **11**, 398–403 (1940). Beams, J. W., Young, J. L., and Moore, J. W., *J. Applied Phys.*, **17**, 886–890 (1946). Beams, J. W., *J. Wash. Acad. Sci.*, **37**, 221–241 (1947).

[4] Beams, J. W., Linke, F. W., and Sommer, P., *Rev. Sci. Inst.*, **18**, 57–60 (1947).

[5] Ecker, P. G., Blum, J., and Hiatt, C. W., *Ibid.*, **20**, 799–801 (1949).

[6] Longsworth, L. G., *J. Am. Chem. Soc.*, **69**, 2510–2516 (1947). Kegeles, Gerson, and Gosting, L. J., *Ibid.*, **69**, 2516–2523 (1947). Coulson, C. A., Cox, J. T., Ogston, G. A., and Philpot, J. St. L., *Proc. Roy. Soc.*, **A192**, 382–402 (1948). Ogston, A. G., *Ibid.*, **A196**, 272–285 (1949). Gosting, L. J., Hanson, E. M., Kegeles, G., and Morris, M., *Rev. Sci. Inst.*, **20**, 209–215 (1949). Gosting, L. J., and Morris, Margaret S., *J. Am. Chem. Soc.*, **71**, 1998–2006 (1949).

[7] Harned, H. S., and Nuttall, R. L., *Ibid.*, **69**, 736–740 (1947). Harned, H. S., and Nuttall, R. L., *Ibid.*, **71**, 1460–1463 (1949). Harned, H. S., and Levy, A. L., *Ibid.*, **71**, 2781–2783 (1949).

[8] Philpot, J. St. L., and Cook, G. H., *Research*, **1**, 234–236 (1948).

[9] Lamb, A. B., and Lee, R. E., *J. Am. Chem. Soc.*, **35**, 1666–1693 (1913).

[10] McMeekin, T. L., Groves, M. L., and Hipp, N. J., *Ibid.*, **71**, 3298–3300 (1949).

[11] Trambarulo, Ralph F., Thesis, Department of Chemistry, Yale University, New Haven, Conn. (1949).

[12] Svedberg, T., and Pedersen, K. O., *The Ultracentrifuge*, Oxford University Press, p. 447 (1940).

[13] Mosimann, H., and Signer, R., *Helv. Chim. Acta*, **27**, 1123–1137 (1944).

[14] Wales, Michael, *J. Phys. & Colloid Chem.*, **52**, 235–248 (1948). Wales, M., Williams, J. W., Thompson, J. O., and Ewart, R. H., *Ibid.*, **52**, 983–998 (1948).

[15] Pedersen, Kai O., *Z. physik. Chem.*, **A170**, 41–61 (1934); *Nature*, **135**, 304–305 (1935).

[16] Drucker, C., *Z. physik. Chem.*, **A180**, 359–377, 378–382 (1937).

[17] Archibald, W. J., *J. Phys. & Colloid Chem.*, **51**, 1204–1214 (1947).

[18] Kegeles, Gerson, *J. Am. Chem. Soc.*, **69**, 1302–1305 (1947).

NATIONAL ACADEMY OF SCIENCES
THE RANCHO SANTA FE CONFERENCE CONCERNING THE EVOLUTION OF THE EARTH

By Louis B. Slichter

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Read before the Academy, April 26, 1950

At the meeting of the National Academy of Sciences in Rochester last October, Dr. Urey presented a paper entitled "On the Origin and Development of the Earth and Other Planets." His discussion was distinguished by its emphasis upon the many physical-chemical aspects of this broad subject. The initiation of the round-table discussion which I am privileged to report was a direct consequence of Dr. Urey's stimulating paper.

This conference, sponsored by the Academy, was held on January 23, 24, and 25 at Rancho Santa Fe, California. The discussion was informal, no prepared papers being presented. The subject, "The Evolution of the Earth," was discussed by a group of twenty-four scientists who represented the pertinent basic fields. Because of the recent stimulating contributions of chemists such as Urey, Latimer, and Harrison Brown, the group contained a high proportion of chemists; there were in fact seven chemists, six geophysicists, five geologists, and suitable representation in astronomy, fluid mechanics, physics, and oceanography.[1]

In every aspect of the discussions, the importance to the thinking of the group, of the contributions from all fields represented, was an outstanding feature. From the wealth of subject matter discussed I have selected a few topics for brief report. In this attempt to report upon the extensive informal discussions of the group, I must not imply that my selection of topics or the conclusions here inferred are necessarily representative of the opinions of the others in this group.

The conference opened with discussion of theories of origin of the solar system. In accordance with recent theories, the earth probably has grown by the accretion of relatively cool materials which were not molten at the outset. The chemists strongly favored the cool type of origin, for otherwise they are unable to account for the presence of water and the relative absence of the noble gases and the low abundance of nitrogen. Other chemical arguments were advanced in favor of the hypothesis of a relatively low temperature (about 300 or 400 degrees Kelvin) during the early growth of the earth. In later stages, some found need of temperatures high enough to produce general incipient melting of the crust, namely 1200–1500°K; but many of the geologists held that such temperatures on a world-wide scale, would have produced more complete layering of the crust and mantle than is observed. Both schools of thought of course agreed in requiring temperatures sufficiently high to produce at least

local melting of the crust or mantle. The question at issue was whether general melting of the crust on a world scale had ever occurred. On either hypothesis it still remains to understand how the iron (adopting the hypothesis of a molten iron core) got to the central core without leaving the mantle completely differentiated. Our conceptions of the development of the primitive earth are, to say the least, obscure. It is even uncertain whether the earth today is cooling or heating at depth, but the odds seem to favor the hypothesis of a heating earth.

The number of rock specimens whose age has been well measured, and the distribution of these specimens with respect to the important Pre-Cambrian structures on this continent, now seems to have arrived at an interesting stage. For the first time large-scale orderly patterns seem to be emerging which foretell the great potential fertility of the radioactive age measurement program. The status of the age determinations was reviewed, and measurements presented concerning eight major orogenic belts of the Pre-Cambrian. The successive positions and directions of these ong linear zones of activity were suggestive of successive stages in an orderly process of growth of the continent. The earliest dated orogeny, an east-west belt in Manitoba, Ontario and Quebec, is about 2.4 bil'ion years old. Yet the geologic record shows that dry land existed in this area at even earlier times. The existence of dry land at the very beginning of the known geologic record is surely a significant point. The age measurements as a group tend to confirm the thesis of recurrent orogenic activity in the earliest geologic era of a type not basically different from that which is so well observed in recent geologic time.

It has generally been held that the *quantity* of radioactive heat production in the crust amply suffices to meet the energy requirements of the earth's internal geological machinery. This view was, I believe, the generally accepted view at the conference. However, the important question remains—by what processes is this heat energy converted to the mechanical work of mountain building or continent building revealed in the geologic record?

The traditional basic mechanism for mountain building is the shrinking of a cooling earth. At our conference, however, many seemed to place faith in the alternative hypothesis of a heating earth; accordingly another method was needed for producing mountains and continents. The following process which seems to offer the ingredients for a suitable self-propagating mechanism was proposed and discussed. At a depth, the thick mantle of the earth probably has the approximate composition of stony meteorites or of peridotite. Bowen's classical studies at the Carnegie Geophysical Laboratory indicate that in a heating melt of peridotitic composition, the last crystals to melt are olivine and hypersthene, of high density. In a large magma chamber heating slowly, these will settle through the liquid

to form the ultra-basic rock known as dunite at the bottom of the chamber. The lighter fraction has a composition similar to that of the continental crust. The low melting components (alkalis) and radioactive elements are incorporated in this fraction; and this fraction can differentiate further depending on the history of cooling to form all the variety of igneous rocks which are known on the surface of the earth. A separation of radioactive materials by transport upward would produce smaller temperature grad ents and more uniform temperatures below.

The establishment of lower temperature gradients would increase the size of the temperature zone favorable for the incipient process of fractionation. Thus the differentiation would tend to encompass larger and larger volumes; it would in brief, tend to be self-propagating. A tendency for mountain building or continent building is obviously associated with such a process; namely, the tendency for the heavier dunite to sink and thereby initiate convective motion, and the tendency for the lighter fraction to rise.

The hypothesis of an essentially basaltic continent floating, so to speak, on a denser ultra-basic material is of course a very old one, but recent seismic evidence seems to furnish important new support to this concept. Under continents the major seismic discontinuity in the outer crust, known as the Mohorovičić discontinuity, usually occurs at depths of between 25 and 40 km. Beneath this discontinuity, occur rocks characterized by notably higher wave velocities, generally assumed to be ultra-basic. This discontinuity has been widely recognized under the continents, wherever seismic observations are available. However, Ewing's new seismic observations in the deep Atlantic basin, indicate the absence of this discontinuity and the absence of the thick basaltic layer under the Atlantic ocean. Instead, Ewing finds that the characteristic high velocity rocks occur close to the sea bottom, and thus at a much higher elevation. This configuration of the upper surface of the high velocity rocks, with a depression under the continents, is just about what is required to explain the isostatic balance between continents and ocean basins. The density difference between basalt and peridotite, and the thickness of the lighter continental layer of basalt are such as to satisfy Archimedes' requirements for hydrostatic equilibrium.

During the conference, important evidence was presented concerning the growth of the oceans and of the atmosphere throughout geologic time. But this material, so I understand, will be the subject of an early paper by Dr. Rubey; and I shall therefore not attempt to review this large subject now.

Such a conference seems to provide almost the ideal method for stimulating progress and for consolidating the thinking in so broad and complex a subject. The contributions from all the fields represented were almost

equally important and significant. In the words of one of our members "One of the striking results of the conference seemed to be the emergence of general agreement concerning the ideas presented, and the way these all point to a reasonable hypothesis for the growth of the continents." The values in a round table of this type probably cannot be fully recognized at once. But the ideas discussed, will, I believe, develop and mature over a period of years, stimulated at appropriate intervals, let us hope, by similar meetings from broad fields of science.

[6] The Institute's address is Los Angeles 24, California.

[1] Because of travel costs from the east a high percentage of this number came from California. Those attending the conference were: Norman L. Bowen, Harrison Brown, Perry Byerly, Carl Eckart, Maurice Ewing, James Gilluly, Edward Goldberg, David Griggs, B. Gutenberg, P. M. Hurley, J. G. Kirkwood, Adolph Knopf, W. M. Latimer, W. G. McMillan, Linus Pauling, Roger Revelle, H. P. Robertson, W. W. Rubey, L. B. Slichter, Edward Teller, Harold C. Urey, J. Verhoogen, Theodore von Kármán, F. L. Whipple, Oliver Wulf.

The National Academy of Sciences defrayed about 65 per cent of the cost of the conference and the Institute of Geophysics about 35 per cent.

In adjourning the conference, Dr. Pauling offered a motion requesting the chairman to circulate a list of names and addresses of those present in order that they might conveniently exchange reprints or other information, and possibly continue some of the unfinished discussions of the conference by correspondence.

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